CHEMICAL TECHNOLOGY AND ANALYSIS

OF

OILS, FATS, AND WAXES

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PREFACE TO THE THIRD EDITION

THE present work is nominally the third edition of my "*Chemical Analysis of Oils, Fats, and Waxes, and the Commercial Products derived therefrom.*" Practically it is a new work, for not only has the last edition been entirely rewritten, but it has also been expanded into a chemical technology of the subject. This extension of its scope will justify the change of title.

The analytical portion, which in the previous editions constituted the most prominent feature of the work, now forms the main portion of the first volume of this book, whilst the technology of the subject has been relegated to the second volume.

The first three chapters of Volume I. form a general introduction to both the analytical and technical portions of the work. Whilst I have given the amplest consideration to the scientific principles underlying the analytical and technical operations, I have kept prominently in the foreground the practical purposes which this work is intended to serve. Very frequent references have therefore been made in these chapters to the analytical methods and technical processes which form the main subjects of the present work. This especially holds good of the second chapter treating of the theoretical side of the hydrolysis (or saponification) of oils and fats, and also of that portion of the third chapter which deals with the hydrolysis of soap. I hope that the new form in which the matter is presented may serve as an outline of the theory underlying the large industries described in Volume II.

The great impetus which analytical investigations have given to the development of this branch of chemical technology rendered it necessary to devote ample space to the analysis of oils and fats. Hence the technical methods of preparing the raw material which is

subjected to chemical analysis in the laboratory have been transferred to the second volume.

The chapters which in the former editions of this work dealt with the analysis have been entirely recast, and rearranged in such a manner as to provide all the information required by the analyst and by the technical chemist in a synoptical form. With this object in view I have presented all recorded numbers and observations as far as possible in tabular arrangement. The division of the most important numerical values into "*constants*" and "*variables*," outlined in my *Laboratory Companion*, has been strictly carried through in this work, as I consider that only the constants furnish values which are characteristic of the nature of an oil or fat, whereas the variables are merely determinants of their quality. I have further endeavoured to so arrange the analytical portion as to set before the reader a systematic course of analytical examination, the several methods being described in logical sequence. For the sake of convenience I have briefly recapitulated this systematic course in Chapter XI., illustrating it by means of a few examples.

It need hardly be pointed out that all the new analytical matter which has accumulated since the publication of the last edition has been embodied in the work. Obsolete methods and obviously unreliable processes have been omitted, my object being to offer, as far as I am able, to the analyst and technical chemist guidance and assistance such as the reader looks for in a work of this kind. The ideal course of presenting one method only is not yet feasible. Therefore, I have ventured to criticise somewhat freely when several processes had to be described, and to point out certain defects. Wherever possible I have added to my critical remarks suggestions for improvement. I feel that the weight of some practical experience attaches to such criticism as I offer, for the great majority of the methods described here have been tested repeatedly by myself and a number of younger colleagues in my laboratory during the last twenty years.

In the last chapter of the first volume I have collated a number of methods and suggestions which up till now bear a strictly scientific character, but may in the future be worked out into useful analytical processes.

The second volume is specially devoted to the technology of oils

and fats. A detailed description of each individual raw material has been given in Chapter XIV. I have summarised the knowledge we possess at present of each individual oil, fat, and wax, describing its occurrence, mode of preparation, mode of purification, chemical composition, examination and detection of adulterants, and pointing out its technical uses. Thus this chapter furnishes, in a concise form, a series of monographs of all known oils, fats, and waxes.

The manufacturing processes practised in the oil and fat industries have been enumerated in systematic order in the last two chapters. Chief stress has been laid on the exposition of the principles on which the individual industries are based. Wherever it appeared necessary I have added illustrations of apparatus. Most of these have been engraved especially for this edition, and those that are not new have been mostly redrawn. The processes described are those which I know from experience to be in practical use at the present day. Antiquated processes have only been touched upon in the briefest manner, when their description was deemed necessary for the proper understanding of more modern methods. The patent literature has, therefore, only been referred to in so far as it furnishes information of practical importance or contains suggestions for industrial application. It is, of course, impossible to teach the art of successful manufacture, for this must be learnt in the school of experience. In this section of the work the scope for criticism naturally became restricted. The reasons for this are obvious. Moreover, the difficulty of judging is enhanced by the fact that a manufacturing process, which is carried out with advantage in one factory, is not infrequently a failure in another.

Throughout the two volumes of the work there will be found interspersed a considerable number of original notes which I have not published hitherto.

In order to increase the utility of the book I have given numerous cross-references in its pages, and have added a somewhat comprehensive index of subject matter.

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CHAPTER I

CLASSIFICATION OF OILS, FATS, AND WAXES — PHYSICAL AND CHEMICAL PROPERTIES OF OILS, FATS, AND WAXES

THE fatty oils (liquid fats), solid fats, and waxes which are the subject of this treatise are found ready formed in vegetable and animal organisms. The discussion of the theories put forward to explain the synthesis of these substances in plants and animals lies beyond the scope of this work, and the reader must be referred for further information to text-books on physiology.

Under the term fats and waxes (liquid and solid) we comprise all those naturally formed substances which consist mostly of glycyl- or other esters of the higher members of the several series of fatty (aliphatic) acids, with which in some cases notable amounts of the free fatty acids themselves and free alcohols are admixed.

In the present state of our knowledge, a strictly systematic classification of fats and waxes is not possible. In older text-books, various attempts have been made to establish several classes or groups, differing chiefly by some physical properties. Thus the consistence has been made the basis of a classification into oils, butters, and solid fats; but as the consistence depends on the mean annual temperature, a substance like cocoa nut oil would be a solid fat in a temperate climate, whereas, in its place of origin, it is of an oily consistence, as its name implies. It would be easy to multiply examples of this kind, demonstrating the inadmissibility of such a principle of classification. Again, some authors have endeavoured to differentiate the fats into several groups on the strength of some prominent chemical property of the fatty oils, such as their drying power; but here also the old adage "*natura non facit saltum*" proves too strong for an artificial classification, inasmuch as there exist a number of fatty oils, occupying an intermediate position, so that they might be classed under two or more heads.

A rational classification must be founded on distinct physical, as well as chemical properties. Therefore, the attempt will be made in this treatise to base the classification, as far as possible, on such physical and chemical differences as can be readily ascertained by means of analysis.

Such distinct difference can be established between fats (liquid and solid) on the one hand, and waxes on the other, on chemical grounds.

Considered chemically, fats (fatty oils and solid fats) are the neutral glycerides of fatty acids, whereas waxes are esters formed by the union of fatty acids with alcohols, not belonging to the glycerol series. It should be noted, however, that this chemical difference does not always find a ready expression in common parlance. Thus, *e.g.*, Japan wax consists chiefly of glycerides, and would more properly be termed Japan tallow. On the other hand, sperm oil must be classed, according to its chemical constitution, amongst the waxes. It is desirable that the old misleading terms should be gradually deleted from chemical treatises.

The term *wax* is frequently used as a generic name for a number of solid hydrocarbons, *i.e.* mineral waxes. A full description of these does not fall within the purview of this work, and they will only be referred to in connection with the analysis of the fatty products with which they may be admixed, as in the manufacture of certain candles and similar products.

The most convenient classification of fats (fatty oils and solid fats) for practical purposes, appears to be given by arranging them according to the magnitude of the iodine value. This principle leads, without unduly forcing it, to a natural subdivision into liquid fats and solid fats, the former being differentiated from the latter by the considerably higher iodine value. Hence, an arrangement based on the magnitude of the iodine value would include the older system of classification according to consistence. Inasmuch as the magnitude of the iodine value stands in close relationship to the absorption of oxygen, or, in other words, to the drying power, classification on the basis of the iodine value would also include the older subdivision into drying and non-drying oils. For these reasons the iodine value has been made one of the chief determinants in the arrangement of the natural products dealt with in this work.

Recent researches have established the fact that all vegetable fatty oils and fats are characterised by the occurrence of phytosterol (and its congeners), whereas all fatty oils and fats of animal origin contain cholesterol as the corresponding alcohol. This important distinction naturally leads to a second guiding principle in the subdivision of the glycerides.

Arranging, then, the fatty oils and solid fats according to these two principles, we obtain the following subdivision :—

I. Liquid Fats or Fatty Oils

A. Vegetable oils.

1. Drying oils.
2. Semi-drying oils.
3. Non-drying oils.

B. Animal oils.

1. Marine animal oils.
   - (*a*) Fish oils.
   - (*b*) Liver oils.
   - (*c*) Blubber oils.
2. Terrestrial animal oils.

II. Solid Fats

A. Vegetable fats.

B. Animal fats.
1. Drying fats.
2. Non-drying fats.

For the classification of the waxes, we can, in our present state of knowledge, adopt the iodine value only as a basis for subdivision; so far, it is not yet possible to establish a distinction, based on chemical properties, between vegetable[1] and animal waxes. However, for the sake of uniformity it may be convenient to carry through the subdivision on the same lines as adopted above for the fats. We arrive, therefore, at the following classification:—

I. Liquid Waxes.

II. Solid Waxes.
A. Vegetable waxes.
B. Animal waxes.

I. Fats (Liquid Fats, or Fatty Oils, and Solid Fats)

1. Chemical Constitution of Fats—Preparation and Properties of Pure Glycerides

The fats are the product of the combination of glycerol and fatty acids. Glycerol being a trihydric alcohol, and consequently deporting itself like a trihydric base, is able to combine with three radicles of fatty acids, as expressed by the following equation, in which R represents the acid radicle of any fatty acid:—

$$C_3H_5\begin{matrix}O.H\\O.H\\O.H\end{matrix}+3R.OH=C_3H_5\begin{matrix}O.R\\O.R\\O.R\end{matrix}+3H_2O.$$

The resulting compounds are called "triglycerides" or "neutral glycyl esters," and they may be compared to neutral salts; therefore the triglycerides are also called *neutral fats*, and their nomenclature is similar to that of salts. Thus we speak of glyceryl stearate or stearic glyceride, etc. This constitution of the fats has been established by the classic researches of *Chevreul* (*Les Corps Gras d'origine animale.* Paris, 1815-1823. Reprinted 1889), *Berthelot*, and *Wurtz.*

Adopting this constitution of the neutral fats, theory predicts the possible existence of monoglycerides and diglycerides corresponding to the formulæ

$$C_3H_5\begin{matrix}O.R\\O.H\\O.H\end{matrix} \text{ and } C_3H_5\begin{matrix}O.R\\O.R\\O.H\end{matrix}$$

[1] Phytosterol has been shown to occur in flax-wax. C. Hoffmeister, *Berichte*, 1903, 1047.

In nature apparently only the triglycerides occur; the monoglycerides and diglycerides are, as a rule, not met with in freshly prepared fats. True, *Reimer* and *Will*[1] have found in old rape oil the diglyceride of erucic acid, $C_3H_5(O.C_{22}H_{41}O)_2(OH)$, but this exception to the general rule is only an apparent one, as it is most likely that the rape oil in question had become rancid with formation of free erucic acid, whilst dierucin separated as a solid mass (see p. 26).

The monoglycerides and diglycerides are obtained synthetically by the following two general methods. *Berthelot's*[2] method consists in heating together fatty acids with glycerol in a sealed tube. Inasmuch as it is difficult to so control the reaction that only a monoglyceride or a diglyceride be formed, it will be found more convenient to employ the following method:—Mix equivalent quantities of α-monochlorhydrin in the case of monoglycerides and α-dichlorhydrin or β-dibromhydrin in the case of diglycerides with the finely powdered sodium salts of the fatty acids (*Romburgh*,[3] *Guth*[4]), and heat the mixture. The sodium chloride formed separates at the bottom of the vessel. The glyceride is then extracted with ether, and filtered over charcoal. (See Appendix.)

Monoglycerides

According to the position which the fatty acid radicle occupies in the molecule, two isomeric monoglycerides are possible, as explained by the following formulæ, in which R denotes the fatty acid radicle:—

$$C_3H_5\begin{matrix}O.R\\O.H\\O.H\end{matrix} \quad \text{or} \quad C_3H_5\begin{matrix}O.H\\O.R\\O.H\end{matrix}$$

The compounds corresponding to the first formula will be denoted as α-compounds.

The following monoglycerides have been prepared hitherto:—

Monoformin, $C_3H_5(O.CHO)(OH)_2$, is obtained by heating monochlorhydrin with sodium formate to 160° C. It is also formed when oxalic acid is heated together with glycerol to 190° C. Monoformin boils *in vacuo* at 165° C.

Monoacetin,[5] $C_3H_5(O.C_2H_3O)(OH)_2$, is obtained together with diacetin and triacetin on heating anhydrous glycerin with glacial acetic acid. It is a thick liquid, easily soluble in water and alcohol, very sparingly soluble in ether, and almost insoluble in benzene. Monoacetin is very hygroscopic; its specific gravity is 1·2212 at 15° C. (water of 15° C. = 1). It boils without decomposition at 130°-132° C. under a pressure of 2-3 mm. At higher pressures it is decomposed.

1 *Berichte*, 1886, 3320.
2 *Chimie organique fondée sur la synthèse.* Paris, 1860, vol. ii.
3 *Recueil des Travaux chimiques des Pays Bas*, 1882, 186.
4 *Zeit. f. Biologie*, 14, 78.
5 Geitel, *Journ. prakt. Chem.* 1897 (55), 422, 425.

α-Monobutyrin,[1] $C_3H_5(O.C_4H_7O)(OH)_2$, is formed on heating together equivalent proportions of sodium butyrate and α-monochlorhydrin. It is an oily, colourless liquid of the specific gravity 1·008 at 17° C.; it boils under the ordinary pressure at 269°-271° C., and under a pressure of 16 mm. at 160°-163° C. In the butyro-refractometer it indicates 26 "degrees" at 40° C. Monobutyrin is less soluble in water than monoacetin; 8 volumes of monobutyrin are miscible with 3 volumes of water; with 5 or more volumes of water an emulsion is formed.

Monoisovalerin, $C_3H_5(O.C_5H_9O)(OH)_2$, is obtained by *Berthelot's* reaction on heating isovaleric acid with glycerol to 200° C. It is an oily liquid of the specific gravity 1·000 at 16° C. One volume of monoisovalerin forms with half a volume of water a clear liquid, but on addition of another half a volume or more of water, the monoglyceride is precipitated. (See Appendix.)

α-Monopalmitin, $C_3H_5(O.C_{16}H_{31}O)(OH)_2$. The glyceride prepared by the two methods mentioned above, had the melting points 53° C. (*Chittenden* and *Smith*[2]) and 65° respectively. One hundred parts of absolute alcohol dissolve at 22·5° C. 5·306 parts. The refraction in *Zeiss'* butyro-refractometer is 25·3 "degrees" at 75° C. (See Appendix.)

α-Monostearin, $C_3H_5(O.C_{18}H_{35}O)(OH)_2$, obtained by the second method described above, melts at 73° C. (*Guth*). It crystallises in microscopic needles. In heated alcohol and hot ether it dissolves easily, but only sparingly in cold ether. It distils unchanged *in vacuo*. The butyro-refractometer index is 28·8 "degrees" at 75° C.

Monoarachin, $C_3H_5(O.C_{20}H_{39}O)(OH)_2$. It is nearly insoluble in cold ether.

Monocerotin, $C_3H_5(O.C_{26}H_{51}O)(OH)_2$, forms long, fine needles, melting at 78·8° C. (*Marie*).[3]

Monomelissin, $C_3H_5(O.C_{30}H_{59}O)(OH)_2$. Melting point 91·5°-92° C.

α-Monoolein, $C_3H_5(O.C_{18}H_{33}O)(OH)_2$, is a yellowish liquid, solidifying at 0° C. to a white mass; on standing it solidifies slowly at the ordinary temperature (from 15° to 20° C.). It decomposes on being distilled *in vacuo*. Its refraction in the butyro-refractometer is 60·1 "degrees" at 40° C. (See Appendix.)

Diglycerides

Theoretically, two isomeric diglycerides containing the same fatty acid radicle are possible, as indicated by the following two formulæ, in which R denotes the fatty acid radicle :—

$$C_3H_5\begin{array}{l}O.R\\O.H\\O.R\end{array} \text{ or } C_3H_5\begin{array}{l}O.R\\O.R\\O.H.\end{array}$$

The compounds conforming to the first formula will be denoted α-glycerides; they are prepared from α-dichlorhydrin and the salts of

[1] α-Monoisobutyrin boils at 264°-266° C. under ordinary pressure; at 158°-161° C. under 16 mm. pressure. In the butyro-refractometer it indicates 21·2 "degrees" at 40° C.

[2] *Amer. Chem. Journ.* 6, 225.

[3] *Annal. de Chimie et de Phys.* 7, 202.

fatty acids. The compounds corresponding to the latter formula will be termed β-glycerides; they are prepared in a corresponding manner from β-dibromhydrin.

Diformin, $C_3H_5(O.CHO)_2(OH)$. Its specific gravity is 1·304 at 15° C.; and the boiling point under a pressure of 20-30 mm. 163°-166° C.

Diacetin, $C_3H_5(O.C_2H_3O)_2(OH)$, is formed together with monoacetin and triacetin on heating anhydrous glycerin with glacial acetic acid. It boils, under 40 mm. pressure, at 175°-176° C. without decomposition. Its specific gravity is 1·1769-1·1788 at 15° C. (water at 15° = 1). It is easily soluble in water and alcohol, less readily in ether, and with more difficulty still in benzene. Diacetin is a commercial product, and has been used latterly as an adulterant of essential oils.[1]

α-Dibutyrin,[2] $C_3H_5(O.C_4H_7O)(OH)(O.C_4H_7O)$. The specific gravity of the substance as prepared by *Berthelot* was 1·083 at 17° C. It boils under a pressure of 19 mm. at 173°-176° C., and under atmospheric pressure at 279°-282° C. The refraction in the butyro-refractometer is 14 "degrees" at 40° C.

β Dibutyrin,[3] $C_3H_5(O.C_4H_7O)(O.C_4H_7O)(OH)$, boils under a pressure of 19 mm. at 166°-168° C., and under atmospheric pressure at 273°-275° C. Its refraction in the butyro-refractometer is 18 "degrees" at 40° C.

Diisovalerin, $C_3H_5(O.C_5H_9O)_2(OH)$. Its specific gravity is 1·059 at 16° C.

α-Dipalmitin, $C_3H_5(O.C_{16}H_{31}O)(OH)(O.C_{16}H_{31}O)$. The dipalmitin of the melting point 59° C., obtained by *Berthelot* on heating glycerol and palmitic acid, as also the dipalmitin of the melting point 61° C., obtained by *Chittenden* and *Smith*, are most likely identical with the product obtained by *Guth* on heating two molecules of sodium palmitate with one molecule of α-dichlorhydrin. Provided that no molecular rearrangement takes place on heating, the constitution of this compound must be that of an α-monoglyceride. It melts at 69° C., and in the butyro-refractometer it indicates 23·8 "degrees" at 75° C.

β-Dipalmitin, $C_3H_5(O.C_{16}H_{31}O)(O.C_{16}H_{31}O)(OH)$, has been obtained from sodium palmitate and β-dibromhydrin. This compound melts at 67° C., and indicates in the butyro-refractometer 21·8 "degrees" at 75° C.

α-Distearin, $C_3H_5(O.C_{18}H_{35}O)(OH)(O.C_{18}H_{35}O)$. The compound obtained by *Berthelot* (1) on heating 1 part of monostearin with 3 parts of stearic acid to 260° C. for three hours; (2) on heating stearin with an excess of glycerol to 220° C. for twenty-two hours;

[1] *Journ. Soc. Chem. Ind.* 1903, 570.

[2] α-Diisobutyrin boils under ordinary pressure at 272°-275° C., under 22 mm. pressure at 164°-167° C. In the butyro-refractometer it indicates 10·3 "degrees" at 40° C.

[3] β-Diisobutyrin boils under ordinary pressure at 269°-272° C., under 20 mm. pressure at 159°-162° C. In the butyro-refractometer it indicates 11·5 "degrees" at 40° C.

(3) on heating equal parts of glycerol and stearic acid to 160° C. for fourteen hours, having a melting point 58° C., as also the distearin obtained by *Hundeshagen*[1] of the melting point 76·5° C., is very likely the α-compound. *Guth* synthesised the α-distearin by heating one molecule of α-dichlorhydrin with two molecules of sodium stearate in a sealed tube to 140°-150° C. for 6 to 8 hours. This distearin crystallises from petroleum ether in rhombic plates, melting at 72·5° C. In the butyro-refractometer it indicates 25·3 "degrees" at 75° C.

β-Distearin, $C_3H_5(O.C_{18}H_{35}O)(O.C_{18}H_{35}O)(OH)$, is obtained from one molecule of β-dibromhydrin and two molecules of sodium stearate. It crystallises from petroleum ether in prismatic plates, of the melting point 74·5° C. In the butyro-refractometer it shows 25 "degrees" at 75° C.

Diarachin, $C_3H_5(O.C_{20}H_{39}O)_2(OH)$, melts at 75° C.; it is almost insoluble in cold ether, but very readily soluble in carbon disulphide.

Dicerotin, $C_3H_5(O.C_{26}H_{51}O)_2(OH)$, melts at 79·5° C.; it is almost insoluble in boiling alcohol.

Dimelissin, $C_3H_5(O.C_{30}H_{59}O)_2(OH)$, melts at 90° C.

α-Diolein, $C_3H_5(O.C_{18}H_{33}O)(OH)(O.C_{18}H_{33}O)$. The compound obtained by *Berthelot* on heating 1 part of monoolein with 5 parts of oleic acid to 250° C. for several hours, or on heating olein with glycerol to 200° C. for 22 hours, is most likely the α-compound. The true α-diolein was prepared by *Guth* from α-dichlorhydrin and sodium oleate. α-diolein differs very little in its physical properties from α-monoolein. Like the latter it solidifies at 0° C. to a white mass, which is converted after a few days at the ordinary temperature to a translucent mass, containing white granular particles. In the butyro-refractometer it indicates 58·8 "degrees" at 40° C.

β-Diolein, $C_3H_5(O.C_{18}H_{33}O)(O.C_{18}H_{33}O)(OH)$, is prepared from β-dibromhydrin and sodium oleic. It resembles the α-compound in colour, smell, and taste; it also solidifies at 0° C., but differs from the α-compound in that it remains liquid at the ordinary temperature, even if it be allowed to stand for several weeks. In the butyro-refractometer it indicates 56·3 "degrees" at 40° C.

Dierucin, $C_3H_5(O.C_{22}H_{41}O)_2(OH)$, melts at 47° C. It is almost insoluble in ether and petroleum ether. Its occurrence in old rape oil has been pointed out above.

Dibrassidin, $C_3H_5(O.C_{22}H_{41}O)_2(OH)$, melts at 67° C.; it dissolves with difficulty in ether.

Triglycerides

Theory predicts the existence of two classes of triglycerides, according as in the molecule all three fatty acid radicles have the same or a different composition. The former may be termed *simple triglycerides*, whereas the latter are suitably denominated *mixed tri-*

[1] *Journ. prakt. Chem.* 28, 227.

glycerides. In the former class only one representative can exist for each fatty acid, namely,

$$C_3H_5\begin{matrix} O \cdot R \\ O \cdot R \\ O \cdot R, \end{matrix}$$

whereas in the second class two isomeric triglycerides may be expected in the case of two different acid radicles, and three isomerides in the case of all three acid radicles being different, as explained by the following formulæ :—

$$C_3H_5\begin{matrix} O \cdot R_1 \\ O \cdot R_2 \\ O \cdot R_2 \end{matrix}; \; C_3H_5\begin{matrix} O \cdot R_2 \\ O \cdot R_1 \\ O \cdot R_2 \end{matrix}; \; C_3H_5\begin{matrix} O \cdot R_1 \\ O \cdot R_2 \\ O \cdot R_3 \end{matrix}; \; C_3H_5\begin{matrix} O \cdot R_2 \\ O \cdot R_1 \\ O \cdot R_3 \end{matrix}; \; C_3H_5\begin{matrix} O \cdot R_1 \\ O \cdot R_3 \\ O \cdot R_2. \end{matrix}$$

Until recently most of the natural fats were considered to be mixtures of simple triglycerides of the several fatty acids, say of tripalmitin, tristearin, and triolein, these being the most frequently occurring triglycerides. In favour of this assumption it was maintained that on cooling liquid fats, tripalmitin and tristearin separated out either in their pure state or as a mixture. The theoretical postulate, that there should be in existence also mixed glycerides, had up to lately obtained but very slender support through the experiments of *Bell* and *Lewin* (see "Butter Fat," chap. xiv.), who stated that in cow butter probably oleopalmito-butyrate, of the formula

$$C_3H_5(O \cdot C_{18}H_{33}O)(O \cdot C_{16}H_{31}O)(O \cdot C_4H_7O),$$

occurred. But since *Heise*[1] discovered oleodistearin in Mkányi fat and in kokum butter, other experimenters have isolated a considerable number of mixed triglycerides from natural fats.

The preparation of pure triglycerides from natural products is a very laborious task, and has not always been accomplished satisfactorily, owing to the great difficulty of separating the various triglycerides. Hence, for the preparation of pure triglycerides, synthetical methods must be employed. (See Appendix.)

The pure triglycerides were first obtained by *Berthelot* on heating glycerol with fatty acids. As has been explained already, monoglycerides and diglycerides are formed simultaneously. In order to exclude the formation of the latter, *Scheij*[2] heated glycerol with an excess of fatty acid, and with a view to obtaining complete esterification by removing the resulting water, a slow current of air was passed through the reacting mass. In the case of the triglycerides of the lower acids, a small quantity of fatty acids distils over simultaneously with the water, and it is therefore necessary to add, from time to time, a fresh quantity of acid to the mixture of glycerol and fatty acid. In the case of the higher fatty acids, the completion of the reaction is indicated by the cessation of the evolution of water.

The pure glycerides may also be prepared by heating together

[1] *Arbeiten aus dem Kaiserlichen Gesundheitsamte*, 1896, xii. 540 ; xiii. 302.

[2] *Rec. d. trav. chim. d. Pays-Bas*, 18, 169.

the sodium (or silver) salts of the fatty acids with tribromhydrin (*Guth; Partheil* and *v. Velsen*[1]).

The property of exhibiting a so-called double melting point has been looked upon as characteristic of the triglycerides (as also of the natural fats which constitute mixtures thereof). A number of observers have stated that the triglycerides melt at a certain degree of temperature, then solidify at a higher degree, to melt again on further heating. This curious behaviour was hitherto explained by assuming the existence of two modifications (*Duffy; Heintz*). The matter has, however, been recently elucidated by *Guth* in the case of tristearin, for which the two melting points, 55° C. and 71° C., have been observed. *Guth* ascertained that well-crystallised tristearin has only one melting point, viz. 71·5°, and shows the same point even after it has been melted, provided it be kept in the capillary tube for some time after melting. But, if the tristearin was tested shortly after having been melted in the capillary, or if it had been introduced in a liquid state into the capillary and then cooled too rapidly, it showed two melting points. He further ascertained that at the lower temperature the substance would only melt completely when the capillary tube was very narrow, and the quantity of the substance very small; on examining a somewhat larger quantity of tristearin in a comparatively wide capillary tube, complete melting did not occur at the lower temperature, the mass only becoming soft and translucent; it then solidified again and finally melted at 71·5° C. to a clear liquid. The different behaviour of the crystalline tristearin on the one hand, and of the once fused tristearin on the other, may be explained, as *Guth* suggests, by the melted (at 55° C.) and rapidly solidified substance not yet having passed into the crystalline state, and behaving somewhat similarly as would super-cooled water (which has remained liquid below 0° C.) or a super-saturated solution of sodium sulphate. If the substance be then shaken or disturbed by increasing the temperature, it solidifies again to its original state; the latent heat thus set free is sufficient to melt the whole mass, if the quantity be small. If, however, the quantity of the substance be large, the temperature does not suffice to effect the complete melting, since the surrounding water still absorbs the liberated heat. Crystallised tripalmitin, as also stearodipalmitin and palmitodistearin have, as *Guth* has shown, one melting point only, but under similar conditions as stated above for tristearin, they exhibited two melting points.[2]

In further confirmation it may be mentioned that well-crystallised brassidin showed one melting point only, even after it had been heated to about 40° C. above its melting point.

The assumption of the existence of two modifications must therefore be rejected, and it may be accepted as proven that the triglycerides do not possess two melting points, but that the phenomenon of the so-called double melting point is due to a state

[1] *Archiv. d. Pharmacie*, 1900 [238], 267.
[2] *Kreis* and *Hafner* confirm *Guth's* observations; *Berichte*, 1903, 1125.

of instability, say, to the super-cooling of the once melted substance, which has not regained its crystalline state.

The following triglycerides have been obtained in a state of purity:—

Simple Triglycerides

Triacetin, Acetin, $C_3H_5(O \cdot C_2H_3O)_3$, is prepared by heating 20 c.c. of glycerol with 10 c.c. of acetic anhydride and 50 grms. of finely powdered hydrogen potassium sulphate. As soon as a violent reaction sets in, 20 c.c. more of acetic anhydride are added and the mixture boiled for some time. The cooled mass is exhausted by means of ether, and thus a mixture of triacetin and diacetin is obtained, which can be separated into its components by fractional distillation. Triacetin boils at 258°-259° C. under ordinary pressure; at 172°-172·5° C. under 40 mm. pressure. Its specific gravity is 1·1603 at 15° C. (water 15° C. = 1). It is miscible with alcohol, ether, chloroform, benzene; it is, however, insoluble in carbon bisulphide and petroleum ether. In water it is only slightly soluble, 100 c.c. of water dissolving at 15° C. 7·17 grms. triacetin (*Geitel*[1]). $n_D^{15} = 1{\cdot}4328$ (*Partheil* and *v. Velsen*).

Tributyrin, Butyrin,[2] $C_3H_5(O \cdot C_4H_7O)_3$, is obtained on boiling one molecule of glycerol with three molecules of butyric acid for sixty hours (*Lebedeff*); by heating α-dibutyrin with an excess of butyric acid for about twenty hours (*Berthelot, Guth*); by the interaction of tribromhydrin and silver butyrate (*Parthiel* and *v. Velsen*). It is a colourless liquid, not solidifying at − 60° C., and distilling unchanged under the ordinary pressure at 287°-288° C., under a pressure of 24 mm. at 182°-184° C. The following specific gravities have been given by *Scheij*: $d_4^{20} = 1{\cdot}0324$; $d_4^{40} = 1{\cdot}0143$; $d_4^{60} = 0{\cdot}9963$. The following refractive indices are given by *Scheij*: $n_D^{20} = 1{\cdot}48587$; $n_D^{40} = 1{\cdot}42785$; $n_D^{60} = 1{\cdot}42015$. In the butyro-refractometer the butyrin prepared by *Guth* indicated 12 "degrees" at 40° C. Butyrin is nearly insoluble in water, readily soluble in absolute alcohol and in 85 per cent alcohol, as also in the ordinary organic solvents. It occurs chiefly in cow butter, and was looked upon as the characteristic constituent of butter fat. The taste of butyrin is intensely bitter.

Triisovalerin, Isovalerin, $C_3H_5(O \cdot C_5H_9O)_3$, is formed by heating synthetical divalerin with 8-10 parts of isovaleric acid to 220° C. It is soluble in alcohol and ether. Isovalerin is a characteristic constituent of dolphin and porpoise oils.

Tricaproïn, Caproïn, $C_3H_5(O \cdot C_6H_{11}O)_3$, has been prepared synthetically from glycerol and caproic acid. It is a colourless, tasteless, and odourless liquor, freezing at a temperature of about − 60° C.

[1] *Journ. f. prakt. Chemie,* 55, 420.

[2] Triisobutyrin boils under the ordinary pressure at 282°-284° C., under a pressure of 24 mm. at 173°-176° C. In the butyro-refractometer it indicates 10·2 "degrees" at 40° C.

and liquefying at about $-25°$ C. The following constants were determined by *Scheij*:—Specific gravity: $d\frac{20}{4} = 0·9817$; $d\frac{40}{4} = 0·9651$; $d\frac{60}{4} = 0·9494$. Refractive index: $n^{20}_{D} = 1·44265$; $n^{40}_{D} = 1·43502$; $n^{60}_{D} = 1·42715$. It is miscible with 85 per cent alcohol, and the usual organic solvents at the ordinary temperature. Caproin occurs in cow butter and in cocoa nut and palm nut oils.

Tricaprylin, Caprylin, $C_3H_5(O . C_8H_{15}O)_3$, is obtainable by heating glycerol with caprylic acid. Caprylin is a colourless, tasteless, and odourless liquor, solidifying at $-15°$ C. and melting at 8°-8·3° C. Its specific gravity as determined by *Scheij* is: $d\frac{20}{4} = 0·9540$; $d\frac{40}{4} = 0·9382$; $d\frac{60}{4} = 0·9231$; its refractive index: $n^{20}_{D} = 1·44817$; $n^{40}_{D} = 1·44069$; $n^{60}_{D} = 1·43316$. At the ordinary temperature it is miscible with 85 per cent alcohol, as also with the usual organic solvents. Caprylin is a characteristic constituent of cow butter, cocoa nut oil, and palm nut oil.

Tricaprin, Caprin, $C_3H_5(O . C_{10}H_{19}O)_3$, has been prepared synthetically in the same manner as the two preceding glycerides. It forms crystals melting at 31·1° C. Its specific gravity is $d\frac{40}{4} = 0·9205$; $d\frac{60}{4} = 0·9057$; its refractive index $n^{40}_{D} = 1·44461$; $n^{60}_{D} = 1·43697$.

Caprin is soluble in the usual fat solvents, but dissolves sparingly in absolute alcohol at the ordinary temperature; in the hot it is, however, easily soluble in this menstruum. Caprin is a characteristic constituent of cow butter, cocoa nut and palm nut oils.

Trilaurin, Laurin, Laurostearin, $C_3H_5(O . C_{12}H_{23}O)_3$, has been isolated from pichurim beans or laurel oil by boiling the raw material with alcohol. *Scheij* prepared it synthetically from glycerol and lauric acid; and *Partheil* and *v. Velsen* from tribromhydrin and silver laurate. It is stated to occur in the liver fat of a crustacean.[1] It crystallises in needles, melting point 45° C.; 46·4° C. (*Scheij*). After being heated a few degrees above its melting point and allowed to solidify, it exhibits a lower melting point. Its specific gravity is $d\frac{60}{4} = 0·8944$ (*Scheij*); $d\frac{100}{4} = 0·8687$ (*Partheil* and *v. Velsen*); its refractive index is $n^{60}_{D} = 1·44039$. In the butyro-refractometer it indicates 31·5 "degrees" at 45° C.; 29 "degrees" at 50° C., and 24 "degrees" at 60° C. (*Partheil* and *v. Velsen*). Sparingly soluble in cold absolute alcohol, it dissolves readily in ether. Laurin is the characteristic constituent of laurel oil. (See Appendix.)

Trimyristin, Myristin, $C_3H_5(O . C_{14}H_{27}O)_{33}$, occurs in nutmeg butter, in wax from cochineal, and in the seeds of *Virola Venezuelensis*;[2] it has been prepared synthetically by the general method described above. It crystallises from its ethereal solution in laminæ, melting point 56·5° C. (*Scheij*), 54°-55° C. (*Thoms* and *Mannich*). When melted trimyristin is heated to 57°-58° C. it solidifies to a porcelain-like mass, melting at 45°-55° C. On raising the temperature slightly, for a very short time, it solidifies and regains the original melting point, viz., 56·5° C. On warming the porcelain-like mass to 35°-45° C. it softens, becomes milky and solidifies, to melt again at 56·5° C.

[1] *Chem. Zeit.* 1895, 651.
[2] Thoms and Mannich, *Ber. d. deutsch. pharm. Gesellsch.* 1901, 264.

Its specific gravity is $d^{60}_{4} = 0{\cdot}8848$ and its refractive index $n^{60}_{D} = 1{\cdot}44285$. Trimyristin is easily soluble in ether, benzene, chloroform, and hot absolute alcohol.

Tripalmitin, Palmitin, $C_3H_5(O \cdot C_{16}H_{31}O)_3$, has been obtained synthetically by heating (1) monopalmitin or dipalmitin with palmitic acid; (2) a mixture of glycerol and palmitic acid; (3) tribromhydrin with sodium (or silver) palmitate. It dissolves with very great difficulty in cold alcohol, more easily in hot alcohol; it is also sparingly soluble in cold ether; from hot ether it crystallises in needles. The crystals melt at 63°-64° C. (*Chittenden*); 65·1° C. (*Scheij*); 65·5° C. (*Guth*), and solidify at 45°-47° C. If the crystals are heated to 70° C. and allowed to solidify, they then melt a little above 45° C., then solidify again, and finally melt at 65·1° C. The specific gravity at 80° C. is $d^{80}_{4} = 0{\cdot}8657$; the refractive index $n^{80}_{D} = 1{\cdot}43807$. Tripalmitin occurs in most oils and fats; preponderantly so in Japan wax and Myrtle wax.

Tristearin, Stearin, $C_3H_5(O \cdot C_{18}H_{35}O)_3$, is obtained by heating (1) monostearin with 15-20 parts of stearic acid for three hours at 275° C. (*Berthelot*); (2) glycerol with excess of stearic acid (*Scheij*); (3) α-distearin with stearic acid (*Guth*); (4) tribromhydrin and silver or sodium stearate (*Partheil* and *v. Velsen, Guth*). Stearin is a crystalline substance, less soluble in cold alcohol than palmitin; solutions of tristearin in boiling alcohol deposit the dissolved substance nearly completely on cooling. In *cold* ether and *cold* petroleum ether it dissolves sparingly, more readily if the solvents are heated; benzene and chloroform dissolve it readily even in the cold. The stearin obtained by crystallisation from ether melts at 71·6° C. and solidifies at 70° C. to an indistinctly crystalline mass. The crystallised stearin exhibits only one melting point; but when the crystals are heated above this melting point—by at least four degrees—they solidify at about 52° C. to a wax-like substance, melting at 55° C.; on further heating a few degrees above this point, the melting point 71·6° C. is again observed. The explanation of this phenomenon has been given already (p. 9). The specific gravity of a (not quite pure) specimen of stearin in the melted state was found to be 0·9235 at 65·5° C.; *Scheij* gives $d^{80}_{4} = 0{\cdot}8621$. The refractive index $n^{80}_{D} = 1{\cdot}43987$ (*Scheij*). In the butyro-refractometer it indicates 34 "degrees" at 55° C., and 23·5-24·5 "degrees" at 75° C. (*Partheil* and *v. Velsen; Guth*). Stearin distils unchanged *in vacuo*.

Stearin is partially converted into ethyl stearate by boiling with a solution of sodium in absolute alcohol (*Duffy*[1]), or by heating with small quantities of alcoholic potash (*Bouis*[2]). On substituting amyl alcohol for ethyl alcohol, amyl stearate is obtained (cp. p. 55). Stearin occurs chiefly in solid fats.

Triarachin, Arachin, $C_3H_5(O \cdot C_{20}H_{39}O)_3$, prepared by *Berthelot* from diarachin and arachidic acid, is very slightly soluble in ether.

[1] *Journ. Chem. Soc.* 1852, 303. [2] *Compt. rend.* 45, 35.

Tricerotin, Cerotin, $C_3H_5(O.C_{26}H_{51}O)_3$, has been prepared by *Marie* from dicerotin. It crystallises in slender needles, melting at 76·5°-77° C. Cerotin is stated to occur in the fatty oil from *Aspidium Filix mas*.[1]

Trimelissin, Melissin, $C_3H_5(O.C_{30}H_{59}O)_3$, was obtained from dimelissin by *Marie*.[2] Melissin resembles cerotin; its melting point is 89° C. Hitherto it has not been found in nature.

Triolein, Olein, $C_3H_5(O.C_{18}H_{33}O)_3$. This glyceride is obtained by heating glycerol with an excess of oleic acid at 240° C. for four hours (*Berthelot*); it may also be prepared by heating tribromhydrin and sodium oleate in a sealed tube to 180° C. Olein is an almost colourless and tasteless liquid, solidifying at −4° to −5° C. On standing for several weeks, triolein solidifies at the ordinary temperature to an opaque mass (*Guth*). Olein distils *in vacuo* without decomposition; its specific gravity at 15° C. is 0·900. In the butyro-refractometer it indicates 56·5 "degrees" at 40° C. Olein dissolves easily in ether; in absolute alcohol it is more readily soluble than either palmitin or stearin; it is insoluble in dilute alcohol.

Olein combines with concentrated sulphuric acid to form a saturated compound having the formula $(C_3H_5)_2(O.C_{18}H_{34}O.SO_4.C_{18}H_{34}O.O)_3$;[3] this substance is very unstable, and is partly dissociated on treatment with alcohol into H_2SO_4 and α-hydroxystearic acid. Just as oleic acid is converted by nitrous acid into elaïdic acid (p. 107), so is olein converted under the same conditions into elaïdin.

Olein occurs in most oils and fats; in preponderating quantity in the non-drying oils. Coula oil is stated to consist of almost pure olein.[4]

Trielaïdin, Elaïdin, $C_3H_5(O.C_{18}H_{33}O)_3$, crystallises in warts, melting point 32° C. (*Mayer*), 38° C. (*Duffy*). It dissolves readily in ether, but is nearly insoluble in alcohol.

Trierucin, Erucin, $C_3H_5(O.C_{22}H_{41}O)_3$, is prepared by heating dierucin and erucic acid to 300° C. It forms a crystalline mass, having the melting point 31° C. In cold alcohol it is nearly insoluble, but dissolves somewhat easily in boiling absolute alcohol; it dissolves very readily in ether, benzene, and petroleum ether. Nitrous acid converts trierucin into tribrassidin. Erucin is a characteristic constituent of the oils belonging to the rape oil class. The solid constituent of the oil from *Tropæolum majus* is almost pure trierucin (*Gadamer*).[5]

Tribrassidin, Brassidin, $C_3H_5(O.C_{22}H_{41}O)_3$, is a crystalline powder having the melting point 54°-54·5° C. If pure brassidin is heated above its melting point, even to 100° C., it shows, after cooling, the unchanged melting point 54°-54·5° C.

1 *Archiv. d. Pharmacie*, 1898, 655.
2 *Journ. Chem. Soc.* 1896, Abstracts, i. 347.
3 Cp. also Juillard, *Journ. Soc. Chem. Ind.* 1894, 820.
4 *Journ. Soc. Chem. Ind.* 1895, 493.
5 *Archiv. d. Pharmacie*, 1899 (237), 472.

Triricinolein, Ricinolein, $C_3H_5(O . C_{18}H_{33}O_2)_3$, has been synthesised by heating glycerol with an excess of ricinoleic acid to 230° C. for six hours, unchanged glycerol and ricinoleic acid being removed by water and petroleum ether respectively.[1] If, as in *Berthelot's* method, pressure and high temperature be employed, condensation products of mono- and diricinolein are formed, the simplest of which is isomeric with triricinolein, and has the formula $OH . C_{17}H_{32} . COO . C_{17}H_{32} . COO . C_3H_5(C_{17}H_{32} . COOH)_2$.

When triricinolein is heated in a solution of toluene, with or without zinc chloride, it is condensed to several esters, such as that represented by the formula $(OH . C_{17}H_{32} . COO)_2(C_3H_5 . C_{17}H_{32} . CO)_2O$, which differ from triricinolein by their sparing solubility in alcohol and petroleum ether.

H. Meyer[2] describes triricinolein (prepared by heating ricinoleic acid and glycerol in a current of carbonic dioxide to 280°-300° C.) as a colourless oil soluble in 96 per cent alcohol, and in methyl alcohol, miscible with absolute alcohol and glacial acetic acid, sparingly soluble in petroleum ether. It has the specific gravity 0·959-0·984. It is optically active; $[\alpha]_D = +5·16°$. Unlike castor oil, it does not form ricinelaïdin on treating with nitrous acid. On keeping, it is stated by *Meyer* to undergo polymerisation, the molecule becoming doubled or trebled, as indicated by the increase of the specific gravity to 0·988-1·009, and the decrease of the iodine number 71·84 to 44·7 (cp. however, "Castor Oil," chap. xiv.).

Mixed Triglycerides

The mixed triglycerides prepared synthetically were obtained by similar methods to those employed in the preparation of simple triglycerides. However, when oleic acid is allowed to act on distearin or dipalmitin in the manner described for the synthesis of glycerides, very considerable quantities of tristearin and tripalmitin are formed, whilst the yield of oleodistearin and oleodipalmitin is small. Evidently a molecular rearrangement takes place, so that in the attempt to synthesise the mixed glycerides, such as oleodistearin,[3] a considerable yield of tristearin and smaller quantities of oleodistearin are obtained.

Acetodiformin, $C_3H_5(O . C_2H_3O)(O . COH)_2$, has been obtained by the action of the mixed anhydride of formic and acetic acids, $CH_3 . CO . O . CHO$,[4] on glycerol. It is miscible with alcohol and ether in every proportion. $d^0 = 1·249$. It boils, under a pressure of 27 mm., at 157° C.

β-Acetodibutyrin, $C_3H_5(O . C_4H_7O)(O . C_2H_3O)(O . C_4H_7O)$, is obtained by the interaction of acetodichlorhydrin and sodium butyrate, or by the action of α-dibutyrin on acetyl chloride.

[1] Juillard, *Journ. Chem. Soc.* 1895, Abstracts, i. 500.
[2] *Journ. Soc. Chem. Ind.* 1897, 633, 684.
[3] Kreis and Hafner, *Berichte*, 1903, 2766.
[4] *Béhal*, *Compt. rend.* 128, 1460.

β-acetodibutyrin is a colourless oil of faint ethereal smell and aromatic bitter taste. It is miscible with alcohol and ether in every proportion. Under the ordinary pressure it boils at 289°-290° C., and under a pressure of 16 mm. at 173°-175° C. In the butyro-refractometer it indicates 5·3 "degrees" at 40° C.

Myristopalmitoolein, $C_3H_5(O.C_{14}H_{27}O)(O.C_{16}H_{31}O)(O.C_{18}H_{33}O)$, is stated by *Klimont*[1] to occur in cacao butter; the crystals melt at 25°-27° C.

Oleodipalmitin (*Dipalmitoolein*), $C_3H_5(O.C_{18}H_{33}O)(O.C_{16}H_{31}O)_2$, has been isolated from tallow by fractional crystallisation (*Hansen*[2]). It melts at 48° C. An oleodipalmitin melting at 29·2° C. has been obtained by repeated crystallisation of vegetable tallow from acetone (*Klimont*[3]).

Stearodipalmitin (*Dipalmitostearin*), $C_3H_5(O.C_{18}H_{35}O)(O.C_{16}H_{31}O)_2$, has also been obtained from tallow (*Hansen*). It crystallises in scales of silky lustre, melting at 55° C. Although this substance differs in melting point from the two following isomerides, it is very likely identical with one of them.

a-Stearodipalmitin, $C_3H_5(O.C_{18}H_{35}O)(O.C_{16}H_{31}O)_2$, was prepared synthetically by *Guth* from a-monostearin and palmitic acid. It crystallises in long rhombic plates, having the melting point 60° C. In the butyro-refractometer it indicates 27 "degrees" at 75° C.

β-Stearodipalmitin, $C_3H_5(O.C_{16}H_{31}O)(O.C_{18}H_{35}O)(O.C_{16}H_{31}O)$, has been obtained synthetically from a-dipalmitin and stearic acid. It crystallises in laminæ, having the melting point 60° C.; in the butyro-refractometer it indicates 24 "degrees" at 75° C.

Oleodimargarin (*Oleodidaturin*), $C_3H_5(O.C_{18}H_{33}O)(O.C_{17}H_{33}O)_2$, has been isolated from olive oil (*Holde* and *Stange*[4]). Its specific gravity at 15° C. is 0·980; it melts in the crystallised state at 29° C.

Oleopalmitostearin (*Stearopalmitoolein*), $C_3H_5(O.C_{18}H_{33}O)(O.C_{16}H_{31}O)(O.C_{18}H_{35}O)$, as obtained from tallow (*Hansen*) melts at 42° C. The same glyceride isolated from cacao butter by *Klimont*[5] showed the melting point 31°-33° C.

Palmitodistearin (*Distearopalmitin*), $C_3H_5(O.C_{16}H_{31}O)(O.C_{18}H_{35}O)_2$, has been isolated by *Hansen* from tallow. It crystallises in lustrous laminæ, having the melting point 62·5° C. After recrystallisation from amyl alcohol the melting point 66·8° C. was observed. *Kreis* and *Hafner*[6] are of the opinion that the glyceride isolated by *Hansen* is not a chemical individual, but a mixture.

a-Palmitodistearin is obtained synthetically from a-monopalmitin and stearic acid (*Guth*). The melting point of the crystallised substance is 63° C. In the butyro-refractometer it indicates 22·5 "degrees" at 75° C. The palmitodistearin obtained from beef fat and mutton fat, and melting in the crystalline state at 63·5° C., and in the superfused state at 52° C. and 63° C., is identical with a-palmitodistearin; identical with a-palmitodistearin is also the

[1] *Monatshefte f. Chemie*, 1902 (23), 51.
[2] *Arch. f. Hygiene*, 1902 (42), 1.
[3] *Monatshefte f. Chemie*, 1903, 408.
[4] *Berichte*, 1902, 2402.
[5] *Monatshefte f. Chemie*, 1902 (23), 51.
[6] *Berichte*, 1903, 1123.

glyceride obtained from distearin and palmitic acid (*Kreis* and *Hafner*[1]).

Daturodistearin (*Distearodaturin*), $C_3H_5(O \cdot C_{17}H_{33}O)(O \cdot C_{18}H_{35}O)_2$, is obtained from lard by crystallisation from ether or petroleum ether solution. It crystallises in large laminæ, appearing under the microscope as plates. In the crystalline state the melting point is 66·2° C.; in the superfused state 51·8° C., and 66° C. (*Kreis* and *Hafner*[2]).

Oleodistearin, $C_3H_5(O \cdot C_{18}H_{33}O)(O \cdot C_{18}H_{35}O)_2$. This is the first known mixed glyceride. It was obtained by *Heise* from Mkányi fat and kokum butter, by precipitating an ethereal solution of these fats with alcohol. It has further been found in cacao butter (*Fritzweiler*[3]). It melts at 44°-44·5° C. and solidifies at 40·8° C. If the melted glyceride is cooled rapidly, the melting point 27°-28° C. is observed; on further heating, the substance solidifies again, and finally melts at 37°-38° C. The specific gravity at 70° C. is 0·8928, and at 90° 0·8547. The oleodistearin obtained synthetically by the action of oleic acid on α-distearin melts about 2° to 4° C. lower than the natural oleodistearin from Mkányi fat and kokum butter (*Kreis* and *Hafner*).

Elaïdodistearin, $C_3H_5(O \cdot C_{18}H_{33}O)(O \cdot C_{18}H_{35}O)_2$, is obtained by the action of nitrous acid on oleodistearin (*Henriques* and *Künne*[4]). It melts at 61° C.

Dioleostearin, $C_3H_5(O \cdot C_{18}H_{33}O)_2(O \cdot C_{18}H_{35}O)$, has been found recently in human fat (*Partheil and Ferié, Arch. d. Phar.* 1903, 545).

The occurrence of a mixed glyceride of Japanic and palmitic acids having the formula $C_3H_5(C_{20}H_4[CO \cdot O]_2)(O \cdot C_{16}H_{31}O_2)$ in Japan wax is considered probable by *Geitel* and *v. d. Want*.

2. Properties of Natural Oils and Fats

The natural oils and fats may, for practical purposes, be looked upon as mixtures, in varying proportions, of the triglycerides described above. The most important of the triglycerides, because most frequently occurring in nature, are tripalmitin, tristearin, and triolein. In consequence of the discovery of mixed glycerides, the question whether mixed glycerides do occur in the natural fats far more frequently than has been assumed hitherto, has become a very important one, but at present our knowledge is still too limited to justify any definite expression of opinion as to the composition of the glycerides in the oils and fats.

The methods of preparing the various vegetable and animal fats (see chap. xiii.), being comparatively crude ones, the oils and fats generally contain impurities of one kind or another, such as colouring and mucilaginous matter, remnants of vegetable and

[1] *Berichte*, 1903, 1123. [2] *Ibid.* 1903, 2766.
[3] *Arbeiten a. d. Kaiserl. Gesundheitsamte*, 1902, 371.
[4] *Berichte*, 1899, 387.

animal tissues, or other foreign substances. For the most part these can be removed by steaming or washing with water, followed by bleaching and filtering (cp. chap. xiii.). But even after this purification they still contain small quantities of foreign substances such as traces of colouring matters, chromogenic substances (producing the colour reactions which are characteristic of some oils and fats), albuminoid substances[1] in fats of animal origin, or cellulose in oils and fats from vegetable sources. These substances are dissolved in the oils and fats, and appear after saponification, on decomposing the soaps with acid, as flocculent matter between the aqueous and the fatty acid layers.

These foreign substances are comprised in the term "unsaponifiable matter." The proportion of unsaponifiable matter lies between 0·5 and 2 per cent, the higher percentage being exceeded only in the case of marine animal oils. A table stating the amounts of unsaponifiable substances found in the natural oils and fats will be given in Chapter VII.

The most important constituents of the "unsaponifiable matter" are cholesterol and phytosterol, inasmuch as by means of these substances we are enabled to discriminate between vegetable and animal fats. Less important amongst the constituents of the "unsaponifiable matter" is lecithin (see p. 156).

Animal fats, when freshly rendered, contain but very small quantities of free fatty acids. For practical purposes they may therefore be considered as consisting of neutral glycerides. If, however, the fats are exposed to the atmosphere, the formation of notable quantities of fatty acids takes place readily (see below). Fats of vegetable origin mostly contain appreciable quantities of free fatty acids, even in their fresh state. *Rechenberg*[2] showed that the amount of free fatty acids is larger in unripe seeds than in ripe ones. In seeds which have been gathered in the unripe state chemical changes take place, resulting in a decrease of fatty acids with the formation of neutral fats.

The natural glycerides are either liquid at the ordinary temperature or melt at a somewhat elevated temperature. Most solid fats melt at about 50° C.; none remain solid at a temperature exceeding 60° C. On cooling they solidify more or less readily. Tables giving the solidifying and melting points of the natural fats will be found in Chapter V.

If the cooling takes place gradually, solid glycerides separate in a crystalline or semi-crystalline state, so that the liquid portion can be separated mechanically from the solid portion by filtering (filter-pressing). This operation is frequently employed on a large scale as in "demargarinating" edible oils (cotton seed oil) or "racking" oils (cod liver oil) (see chap. xv.). The solid glycerides were, up to recently, looked upon as consisting chiefly of stearin or palmitin or mixtures thereof. Hence, in commerce all solid fats obtained in the

[1] Yssel de Schepper und Geitel, *Dingl. Polyt. Journ.* 245, 295.
[2] *Berichte*, 1881, 2217.

manner described are termed "stearine."[1] In consequence of the discovery of mixed glycerides, this view must be abandoned; further research will most likely show that the "stearines" differ chiefly in their contents of mixed glycerides. A few investigations made in this direction have already led to the isolation of several mixed glycerides from olive oil, cacao butter, mkányi fat, kokum butter, tallow, and lard.

In their liquid state fats easily penetrate into the pores of dry substances; if dropped on paper they leave a transparent spot—grease spot—which cannot be removed by washing with water and subsequent drying (difference from glycerol spots).

Oils and fats are in their pure state odourless, colourless, and tasteless; and what is usually regarded as characteristic in these respects of the different oils and fats, is really due to the presence of small quantities of foreign substances.

A curious effect, which may be used for the detection of the minutest quantities of oils and fats, has been described by *Lightfoot*. Camphor, crushed between layers of paper without having been touched with the fingers, rotates when thrown on water, but a trace of oil or fat on the surface of the water causes the rotation to cease immediately; it is sufficient to touch the water with a needle which has been passed previously through the hair.

The natural oils and fats may be considered as completely insoluble in water, although traces are dissolved when they, especially the oils (liquid fats), are shaken with large quantities of water. On allowing the emulsions thus obtained to become clear by standing, subsequently separating the fat, filtering the aqueous layer, and shaking the latter with ether, a minute quantity of fat will be found to have passed into that solvent, and can be removed by evaporating the ether. On the other hand, oils and fats dissolve a little water; this can be entirely expelled on warming above 100° C.

With the exception of castor oil, all oils and fats dissolve but very sparingly in cold *alcohol*. Boiling alcohol, however, dissolves somewhat larger quantities, especially of those oils and fats which contain glycerides of the lower fatty acids; but on cooling, nearly all the dissolved fat separates out. The solubility is considerably increased by the presence of free fatty acids; if the amount of the latter be large, exceeding say 30 per cent, even cold alcohol will readily effect dissolution.

The oils and fats dissolve very readily in *ether*, *carbon bisulphide*, *chloroform*, *carbon tetrachloride*, *benzene*, *petroleum*, and *petroleum ether*. Castor oil, however, forms an exception as regards the two last-mentioned solvents (cp. "Castor Oil," chap. xiv.). Triacetin is insoluble in carbon bisulphide and petroleum ether. Further information as regards solubility in the solvents mentioned above, as also in other solvents, will be found in Chapter V. p. 213.

[1] Stearin, palmitin, acetin, etc. (spelt without an "e"), denotes in this work the pure triglycerides, whilst under "stearine," "acetine," the commercial products are understood.

The solutions of the neutral fats are without action on indicators, provided, of course, that the solvents used have been completely freed from traces of acids.

Oils and fats dissolve sulphur and phosphorus at the ordinary temperature[1] to a slight extent.[2] They also dissolve small quantities of soaps; the solubility of the latter is considerably increased by the presence of ether and petroleum ether.

The specific gravity of oils and fats is less than that of water; it varies between the limits of 0·910 to 0·970.

The natural fats can be heated to a temperature of about 200° C. or 250° C. without material change, provided prolonged contact with air is avoided. Some oils and fats become lighter in colour in consequence of the destruction of colouring matter dissolved (linseed oil). On being heated above 250° C. up to 300° C. the drying oils undergo a change very likely due to polymerisation. Thus, tung oil (cp. chap. xiv.) is converted into a gelatinous solid mass. The industry of preparing lithographic varnish is based on this reaction (chap. xv.). In the case of castor oil, a chemical change takes place, leading even to the formation of solid products.

When fats are still further heated decomposition sets in, with the formation of volatile products, the most prominent of which is acroleïn. The intense odour of acroleïn, which all fats emit on heating above 300° C., is one of the most characteristic reactions, enabling us to distinguish fatty oils and fats from mineral and ethereal oils. Amongst the volatile products obtained on heating oils and fats to high temperatures are found hydrocarbons of the ethane, ethylene, aromatic series, and perhaps also naphthenes, the quantity of which is considerably increased when the destructive distillation takes place under pressure. This fact lends strong support to the theory that the petroleum hydrocarbons owe their origin to the destruction of animal fats. The vegetable fats in general offer much greater resistance to the conversion into hydrocarbons under pressure than do animal oils and fats.

On exposure to the **atmosphere** oils and fats gradually undergo certain changes. As these changes are of great importance both from a scientific and commercial point of view, it will be necessary to consider them at some length, devoting special attention, first to the influence which light, air, and moisture separately exert, and secondly, to their conjoint effects.

The action of **light**, to the exclusion of air and moisture, has hitherto not been studied thoroughly. It is well known that oils and fats acquire a pale colour, under the influence of insolation, some oils even becoming colourless. The application of insolation to industrial purposes is well exemplified by the bleaching of linseed oil or cod liver oil under glass. Since pure glycerides are themselves colourless, the light can only affect the foreign substances dissolved in them. This is further proved by the fact that insolated cotton seed

[1] At temperatures above 100° C. sulphur interacts with fats (cp. p. 30).
[2] On the solubility of indigo in oils and fats, cp. *Journ. Soc. Chem. Ind.* 1895, 1027.

oil is not reduced so readily by silver nitrate (*Bechi's* test) as cotton seed oil kept in the dark. Other statements as to the effects of light, such as the development of greater heat in Maumené's test by oils exposed to sunlight, or the formation of small amounts of free fatty acids (*Ballantyne*[1]) still require verification, as the air was not excluded rigidly enough in those experiments upon which the conclusions were based; for even in corked bottles kept in direct sunlight, diffusion of air through the cork takes place in the course of time. Hence, the observed changes are most likely due to the joint influence of light and air, and hence also of moisture contained in the latter.

The effect of light on oils to the exclusion of air has been studied by *Ritsert*.[2] His experiments proved that provided air is rigidly excluded, as in sealed glass tubes, even prolonged insolation is incapable of producing a change leading ultimately to rancidity. *Mjoën*[3] also instituted similar experiments, but no definite conclusions can be drawn from them beyond the inference that the chemical change, taking place under the action of light in presence of air, differs from that occurring in absence of light. There is no satisfactory evidence to support the contention that polymerisation of glycerides (*e.g.* in linseed oil) is produced by light alone; it is desirable that our scanty knowledge on this subject be supplemented by systematic study.

The present state of our knowledge does not justify, therefore, the assumption that light alone, to the exclusion of air and moisture, is capable of effecting a chemical change in glycerides.

When considering the effect of **air** we have to clearly discern between the influence of the ordinary atmosphere—which necessarily includes the action of oxygen, moisture, and light (diffused daylight, direct sunlight)—and the influence of dry air, to the exclusion of moisture and light. The effect of the atmosphere on oils and fats varies in a very marked degree with the composition of the glycerides. As a general rule, it may be stated that the greater the iodine absorbing power of an oil or fat (cp. chap. vi. p. 240), the more readily it will absorb oxygen. The chemical change is most marked in the case of drying oils; it becomes gradually less pronounced with the decrease of the iodine absorption, as we pass through the classes of semi-drying oils and non-drying oils down to the solid fats. Marine animal oils occupy a position similar to that of drying oils. The oxygen absorption power of the various oils and fats will be considered at length in Chapter VII.; therefore, a brief statement may suffice here. Drying oils thicken at first and form an elastic skin on the surface. If exposed in sufficiently thin layers, as for instance, if spread on wood or glass, they are finally converted into a transparent, yellowish, flexible substance, insoluble in water, alcohol, and also, to a very large extent, in ether. Whilst this energetic oxidation

[1] *Journ. Soc. Chem. Ind.* 1891, 29.

[2] *Untersuchungen über d. Ranzigwerden der Fette.* Inaug. Dissert. Berlin, 1890.

[3] *Forschungsber. über Lebensmittel*, etc., 1877, 195.

takes place, heat is developed to so high a degree that if the drying takes place in presence of organic substances, in a fine state of division, offering a large surface to the atmosphere (cotton-waste, woollen rags), spontaneous combustion will ensue. The non-drying oils remain more or less unchanged. The semi-drying oils occupy an intermediate position. The gradations between the various classes are, however, by no means so distinct as to warrant the drawing of hard-and-fast dividing lines between the three classes.

Dry air, to the exclusion of moisture and light, has no action on oils and fats, so that if kept protected from exposure to moisture and light they will remain unchanged for practically an indefinite length of time. As it is very difficult to exclude the last traces of moisture in stored oils and fats, a very slight action of the moisture left in them may take place in the manner described in the following paragraph, that is, small amounts of fatty acids will be formed, but no rancidity will set in. This is a matter of common experience, and has been demonstrated by *Lewkowitsch*[1] in the special cases of a linseed oil kept for thirteen years in bulk, and of a sample of cacao butter kept in a sealed bottle for ten years.

The effect of **moisture** (always present in the atmosphere) is a far-reaching one. In order to fully comprehend this effect, it is necessary to consider the action of water on oils and fats.

At temperatures up to about 150° C., water does not attack glycerides, but if the temperature be raised, say, to 200° C. or above, the triglycerides are finally decomposed into their proximate components, glycerol and fatty acids, the elements of water being taken up simultaneously. This is expressed by the following equation (cp. chap. ii. p. 35):—

$$C_3H_5(OR)_3 + 3H.HO = C_3H_5(OH)_3 + 3R.OH.$$

The hydrolysis thus produced at high temperatures is greatly accelerated if the action of the water is assisted by suitable chemical agents. In presence of such agents it is possible to reduce the temperature. Thus, by the employment of concentrated sulphuric acid, the chemical change (considering for the moment merely its ultimate products) may be effected at a temperature of about 120° C. True, some intermediate products are formed, but the full mechanism of the reaction need not concern us here, inasmuch as by boiling with water they are ultimately decomposed into glycerol and fatty acids. The temperature required for the chemical change may be further reduced to about 100° C. by employing strong hydrochloric acid.[2] A still further reduction of temperature can be effected by the introduction of strong bases in alcoholic solution (see chap. ii.).

Finally, the change may be brought about by water even at the ordinary temperature, if naturally occurring ferments, such as

[1] *Journ. Soc. Chem. Ind.* 1899, 557.
[2] Lewkowitsch, *Journ. Soc. Chem. Ind.* 1903, 6.

lipase,[1] steapsin[2] are intermixed with the fats. Fat-splitting enzymes seem to occur generally in the oleaginous seeds, and to play an important part in the utilisation of the fatty reserve products stored in the seeds. During the germination of the seeds, hydrolysis takes place, and free fatty acids are liberated; hence, it appears very likely that the presence of small quantities of free fatty acids which are always found in, even the freshest, vegetable oils and fats (see p. 17), is due to the slight action of these enzymes on the glycerides stored in the seeds. The absence of suitable conditions in the ungerminated seeds would appear to limit the progress of hydrolysis to a very small degree. Such conditions are the presence of slight amounts of dilute mineral acid, or of a strong fatty acid, such as acetic acid. If water acidulated with small quantities of such acids be churned up with oils and fats, and suitable enzymes be introduced, the hydrolysis of the glycerides takes place gradually, and can be carried to a considerable extent. Thus, the ferment contained in castor seed[3] is capable of effecting practically complete hydrolysis in the course of a few days. Similarly acting ferments, such as steapsin, may be reasonably assumed to be contained in the commercial animal fats to a smaller or larger extent, according to the care exercised in the separation of the animal tissue from the rendered fat.

Accepting, then, the occurrence of small quantities of fat-splitting enzymes in the commercial oils and fats as a fact, we shall now be able to understand those changes which oils and fats undergo on exposure to the atmosphere. As is well known, they thereby acquire a disagreeable smell and an acrid taste, and the presence of free, non-volatile fatty acids, as also of small quantities of volatile acids can be observed. We comprise all these changes under the term "rancidity," and we say the oils and fats have become "rancid." In order to arrive at a satisfactory explanation of these changes, I propose to trace the effects of each of these agents in detail, step by step, and to examine how far such explanation agrees with actual observations.

In the presence of moisture the fat-splitting enzymes are enabled to hydrolyse a small proportion of glycerides, so that glycerol and free fatty acids are formed. Hence the first postulate is that free fatty acids should make their appearance.

It is well known that oils and fats, if kept fully protected from light, air, and moisture, retain indefinitely[4] their state of neutrality, whereas if not carefully preserved, as in imperfectly corked bottles, barrels, etc., moist air easily gains access, and free fatty acids, having the same composition as those which are combined with glycerol in the neutral fat, are produced. The quantity of enzymes

[1] Cp. Green, *The Soluble Ferments and Fermentation*. Cambridge, 1899.

[2] Lewkowitsch and Macleod, *Proceedings of the Royal Society*, 72. 31 (1903), cp. chap. ii.

[3] Connstein, Hoyermann, and Wartenberg, *Berichte*, 1902, 3988.

[4] Friedel (*Compt. rend.* 1897, 648) found in the fatty matter buried several thousand years ago in the tombs of Abydos unchanged triglycerides.

in the commercial oils and fats being very small, the amount of hydrolysis so effected will be restricted, hence the proportion of fatty acids in commercial oils and fats, as a rule, does not exceed a few per cent. If, however, the oils and fats be allowed to stand in contact with the organic matter from which they have been obtained, such as the marc of fruits (as in the case of olive oil and palm oil), or animal tissues (as in the case of rough fat), or casein, etc. (as in the case of butter), then the hydrolysis of glycerides increases somewhat rapidly, and may reach very high proportions. Thus the so-called Bagasse olive oils, *i.e.* oils expressed from exposed olive marc, contain as much as 70 per cent free fatty acids. Palm oil may even undergo complete hydrolysis, and hence consist almost exclusively of fatty acids.[1] Also in these cases, we can explain satisfactorily the formation of so high a proportion of fatty acids by the conjoint action of enzymes and water, since both are present in considerable quantities. It appears, therefore, unnecessary to invoke the action of air and light in order to explain the presence of free fatty acids. For it has been frequently observed that the hydrolysis of palm oil continues in the closed barrels in which it is shipped, *i.e.* in the absence of light and also of air, the liberated glycerol separating out (*Geitel*[2]). Further, *Dieterich*[3] has shown in a very instructive series of experiments that free fatty acids are formed very much more rapidly in rough beef fat and pig's fat—containing animal tissues—than in the freshly rendered fat, and that on the addition of 10 per cent of water to both the rough fats and the freshly rendered fats hydrolysis was considerably increased.

I therefore ascribe the primary cause of rancidity, namely, the formation of free fatty acids, to the action of moisture in the presence of enzymes, *i.e.* soluble ferments. It is quite true that both *Ritsert*[4] and *Reinemann*[5] distinctly state that ferments have no share in causing rancidity, but their experiments with regard to this point are not exhaustive enough to prove their case. The occurrence of small quantities of free fatty acids, even in refined oils and fats (edible oils and fats) would then be explained. Yet these oils and fats are by no means rancid. *Heyerdahl*[6] has shown in the case of cod liver oil that addition of its free fatty acids (from 2 per cent downwards) to samples of oils free from rancidity did not impart to the oil a rancid character, although it certainly produced a sharp taste. Further, *Ballantyne*[7] has demonstrated that in many instances free acid is liberated long before the oils have turned rancid (cotton seed oil, linseed oil), whilst in other

[1] Adipocere (cp. chap. xiv. "Human Fat") is another illustration of what may be termed "auto-hydrolysis."

[2] *Journ. f. praktische Chemie*, 1897 [55], 417.

[3] *Chem. Rev.* 1899, 168, 181, 201. Cp. Lewkowitsch, *Jahrbuch d. Chem.* 9 (1899), 351.

[4] *Untersuchungen über d. Ranzigwerden d. Fette.* Inaug. Dissert. Berlin, 1890.

[5] *Centralb. f. Bakteriologie, Parasitenkunde, und Infektionskrankheiten*, 1900, 131.

[6] *Journ. Soc. Chem. Ind.* 1889, 54. Cp. also Besana, *Chem. Zeit.* 1891, 410, and v. Klecki, *Zeit. f. analyt. Chemie*, 1895, 633.

[7] *Journ. Soc. Chem. Ind.* 1891, 29.

instances rancidity sets in and continues for some time, without the liberation of any free acid. *Lewkowitsch*[1] has also shown in the case of a specimen of cacao butter that although the fat contained free fatty acids, it could not be declared rancid.

Hence, rancidity is not due, as is still widely held, to the presence of free fatty acids alone; in other words, rancidity must not be considered as coterminous with acidity. The frequent confounding of these two terms is caused by the fact, that *acid* oils and fats are frequently rancid as well. It is only when oxygen and light gain access to the acid fats, that the conditions favouring the setting in of rancidity are given. Rancidity is rather due to the direct oxidation of the air, assisted and intensified by the exposure to light. Oxygen and light must act simultaneously, either of these agents alone being unable to produce rancidity (*Ritsert*). Hence, the greater the surface offered to the atmosphere, the greater will be their influence.

I therefore define as rancid those oils and fats, the free fatty acids of which have been acted on by the oxygen of the air, in the presence of light. Similar explanations have been given before, and the only new element I can claim here would consist in more emphatically ascribing the initial phase of rancidity, namely, the hydrolysis, to the action of enzymes than has been done hitherto.[2] Thus, to leave out older statements, *Duclaux*[3] has drawn from an experimental research the conclusion that rancidity is due to slight hydrolysis and subsequent action of the oxygen in the air assisted by light. *Geitel*[4] has further elaborated this explanation by laying stress on the influence of moisture in the initial hydrolysis.

Some authors have maintained that rancidity is due to the action of micro-organisms, a view which seems to have been supported by the discovery of living micro-organisms in poppy seed oil (*Kirchner*),[5] and further by a number of observations made on butter. Butter, however, containing as it does a considerable amount of organic, non-fatty substances, cannot be put on the same basis with oils and fats which we are considering, for it is butter *fat* and not butter with which we are concerned here. It is quite true that bacteria decompose fats to a large extent, but they accomplish this only when suitable nutriment is offered to them with the fat. In that case the micro-organisms will grow, and as all the necessary conditions are provided, free play is given to those agencies which produce rancidity. It may, however, be left an open question whether these changes are due to the direct action of the living organisms, or rather to the action of an enzyme produced by them, much as the alcoholic fermentation of sugar can no longer be ascribed to the living sacharomyces cells, but rather to the zymase produced by them.

[1] *Journ. Soc. Chem. Ind.* 1899, 557.

[2] Lewkowitsch. *Journ. Soc. Chem. Ind.* 1903, 68; *Jahrbuch f. Chemie*, 7 (1897), 368; 8 (1898), 392; 9 (1899), 351; 10 (1900), 382; 11 (1901), 360; 12 (1902), 363.

[3] *Annales de l'Institut Pasteur*, 1887; *Compt. rend.* 102, 1077.

[4] *Journ. f. prakt. Chemie*, 1897 [55], 448.

[5] *Berichte der deutsch. botan. Gesellschaft*, 1888, 101.

In confirmation of this view it may be stated that *Duclaux*[1] has proved in an investigation on butter *fat* that micro-organisms play no part in producing rancidity, since the butter fat, being insoluble in water, does not afford sufficient nutriment to the protoplasma of the cells. (Experiments made on butter do not controvert this.) Similar proof has been given by *Ritsert*,[2] who showed that pure lard is not turned rancid by bacteria, be they aërobic or anaërobic, the bacteria introduced into the fat dying quickly.

Liquid fats—oils—more readily turn rancid than solid fats. Whether fats containing glycerides of lower fatty acids (butter fat, cocoa nut oil) are more liable to become rancid than the fats containing glycerides of the higher fatty acids (cacao butter, tallow, etc.) has not yet been decided experimentally. It may, however, be taken as a general rule that the higher the proportion of insoluble saturated fatty acids, and the lower the percentage of unsaturated glycerides in the fat, the smaller will be its liability to turn rancid. This rule, however, appears to break down in the case of cocoa nut oil and Japan wax. Further investigation is necessary to elucidate these points.

Whilst it may then be taken as proven that rancidity is due to the simultaneous action of moisture, oxygen, and light, very little is known as to the actual chemical change the liberated free fatty acids undergo. Although the number of published observations is large, no definite conclusions can be drawn therefrom. Misled by a faulty application of the acetylation test (cp. chap. vi. p. 274), several observers maintained that direct addition of oxygen to the molecule of fatty acids takes place with the formation of hydroxy acids.[3] Besides, *Gröger*[4] has found in a series of experiments extending over four years that the fatty acids isolated from six kinds of exposed fats had been broken down into acids of lower molecular weight, and had not merely absorbed oxygen by a process of addition. The same chemist has shown that in the further process of oxidation the lower acids are oxidised to azelaic and suberic acids. Other observers suggest that it is principally oleic acid that is set free in rancid oils and fats. This opinion has been put forward recently again by *Scala*[5] who isolated from a very rancid olive oil œnanthaldehyde; formic, acetic, butyric, and œnanthic acids, and further, azelaic and suberic acids. However, experiments made by *Thum*[6] with palm oil and rancid olive oil with a view to ascertaining whether palmitic, stearic, and oleic acids are liberated in the same proportion or in a different one to that in which they exist as glycerides in these fats, have proved that the ratio between oleic acid and solid fatty acids is the same in the free as in the combined state. This fact was confirmed in the case of rancid lard by *Spaeth*. The opinion has also been frequently expressed that the bodies

[1] *Annales de l'Institut Pasteur*, 1887; *Compt. rend.* 102, 1077.
[2] *Untersuchungen über d. Ranzigwerden der Fette.* Inaug. Diss. Berlin, 1890.
[3] Cp. Lewkowitsch, *Analyst*, 1899, 328.
[4] *Journ. Soc. Chem. Ind.* 1889, 202.
[5] *Chem. Centr. Blatt.* 1898, 439; Original *Staz. Sperim. agric. ital.* 30, 613.
[6] *Journ. Soc. Chem. Ind.* 1891, 70.

characteristic of rancid fats are aldehydes and similar substances. (œnanthaldehyde, *Scala*). Hence, the usual reagents employed for the detection of aldehydes have been suggested as a means of differentiating rancid fats from acid fats. *Schmid*[1] states that rancid fats give off, in a current of steam, volatile substances, which colour a 1 per cent solution of metaphenylendiamine yellow. I have, however, shown[2] that a distinctly rancid cocoa nut oil did not give the reaction. Hence, all statements as to the presence of aldehydic substances must be accepted with reserve.

With regard to the glycerol, *Gröger*, following the opinion expressed by *Liebig*, concluded that it must suffer oxidation as well as the fatty acids, since he could not detect free glycerol. But in view of the difficulty of ascertaining minute quantities of glycerol, and in further consideration of the possibility, that the hydrolysis of the rancid fats examined by him had only proceeded to the formation of mono- and diglycerides (cp. chap. ii. p. 35), his view cannot be accepted as proven.[3]

In the present state of our knowledge we are still unable to define rancid oils and fats by chemical means, and we must rely on the taste and smell as the best reagents of ascertaining whether a fat is rancid or not.

Some isolated observations regarding the chemical change in rancid fats are given in the following table published by *Lewkowitsch*:[4]—

[1] *Zeit. f. analyt. Chemie*, 1898, 301.

[2] *Jahrbuch f. Chemie*, 8, 392; *Journ. Soc. Chem. Ind.* 1899, 557. Cp. also Lewkowitsch, *Jahrbuch f. Chemie*, 10, 382, criticism on a Paper by I. Nagel, *Amer. Chem. Journ.* 1900 (23), 173.

[3] Friedel (*Compt. rend.* 1897, 648) also concluded from the examination of fat found in the tombs of Abydos that glycerol was oxidised, without, however, adducing any proof for his opinion.

[4] *Analyst*, 1899, 327; cp. also *Journ. Soc. Chem. Ind.* 1899, 557; Sherman and Falk, *Journ. Amer. Chem. Soc.* 1903, 711.

[TABLE

	Fresh.								After Exposure.								
	Original Oil or Fat.		Acetylated Oil or Fat.						Original Oil or Fat.		Acetylated Oil or Fat.						
	I.	II.	III.	IV.	V.		VI.	VII.	VIII.	IX.	X.	XI.	XII.		XIII.	XIV.	XV.
	Saponification Value.	Total Volatile Fatty Acids per Gram in terms of Milligrams KOH.	Saponification Value.	Hehner Value.	Apparent Acetyl Value. Distillation Process.	Apparent Acetyl Value. Filtration Process.	True Acetyl Value.	Difference, III.-I.	Saponification Value.	Total Volatile Fatty Acids per Gram in terms of Milligrams KOH.	Saponification Value.	Hehner Value.	Apparent Acetyl Value. Distillation Process.	Apparent Acetyl Value. Filtration Process.	True Acetyl Value.	Difference, X.-VIII.	Difference, XIII.-VI.
Cotton seed	...	0·1	200·2	95·7	...	{7·4 / 8·0}	7·6	...	193·0	2·1	201·8	94·0	8·3	10·1	7·1	8·8	−0·5
Curcas	198·2	...	...	95·5	7·5	...	...	...	194·2	1·5	200·4	...	...	9·44	7·94	6·2	...
Castor	179·0	0·0	304·1	...	...	146·9	146·9	125·1	180·2	1·8	304·6	...	...	146·6	144·8	124·4	...
Cod liver	186·45	3·6	189·15	...	4·75	...	1·15	2·7	192·7	8·7	199·7	...	...	19·15	10·45	7·0	+9·3
Cacao butter	192·6	0·81	...	...	2·86	2·71	1·97	...	193·1	0·49	...	...	5·0	4·8	4·41	...	+2·44
Tallow	196·2	1·55	200·5	94·75	6·1	6·1	4·55	4·3	200·0	2·9	210·7	93·2	14·5	12·7	10·7	10·7	+6·15
Premier jus	...	0·53	199·6	...	...	3·3	2·72	...	199·8	2·3	206·2	93·6	11·2	8·2	8·9	6·4	+6·18

From this table it will be seen that rancid fats possess higher acetyl numbers than the same fats in the fresh state. Yet the number of experiments made hitherto is too small to be conclusive evidence in favour of my opinion that the "acetyl value" indicates, chemically, rancidity in a more reliable manner than the doubtful colour reactions proposed hitherto. As a further difference between fresh and rancid fats, it has been pointed out that the heat of combustion of the former is considerably lower than that of the fresh fats (*Stohmann* and *Langbein*[1]). This is explained by the higher proportion of oxygen in rancid fats.

If fatty oils be heated to the temperature of boiling water, and air, or better still *oxygen*, be blown through them, oxidation takes place with evolution of so much heat that the oxidation process continues without further heating. On this reaction is based the industry of blown oils (chap. xv.). The most notable change produced by the action of oxygen is an increase of density. The oils thus obtained simulate castor oil in their density and viscosity, but differ from it in that they are soluble in petroleum ether. The similarity to castor oil, as also the high acetyl values of the blown oils, would point to the formation of glycerides of hydroxylated acids, but at the same time considerable amounts of free volatile fatty acids are formed. The fatty oils belonging to the class of semi-drying oils lend themselves specially to the manufacture of blown oils. The non-drying oils are less readily attacked, and solid fats only suffer a change, if heated to a higher temperature (cp. "Oxygen Absorption," p. 305). In the case of drying oils the oxidation process proceeds much further, yielding finally a jelly-like mass, or even a solid elastic mass. This reaction is made use of in the linoleum industry (cp. chap. xv.).

Caustic alkalis hydrolyse the glycerides readily; less readily so the alkaline earths. The chemical reactions involved are of the greatest importance, both for the chemistry and industry of oils and fats; they will therefore especially be treated both from a scientific (chap. ii.) and from a technical point of view (chap. xv.).

Ammonia hydrolyses the oils and fats to some extent under pressure.

Aromatic bases, such as aniline, etc., also hydrolyse oils and fats, on being heated under pressure to 210°. In the case of aniline, the reaction takes place according to the following equation:[2]—

$$C_3H_5(OR)_3 + 3C_6H_5 . NH_2 = C_3H_5(OH)_3 + 3C_6H_5 . NH . R.$$

The action of *concentrated sulphuric acid* on oils and fats leads, in the first instance, to a rise of temperature (Maumené's test, chap. vii.) with evolution of sulphurous acid. If the oil be mixed very gradually with the acid, and at a low temperature, glycerides of a complex constitution are formed. Thus on treating olive oil with concentrated sulphuric acid a compound has been obtained which

[1] *Journ. f. prakt. Chemie*, 42, 361.
[2] Liebreich, D.R.P. 136,274. English Pat. 12,957, 1902.

may be regarded as a mixed glyceride of oleic acid, stearic acid, hydrogen sulphate, and hydroxystearic acid,[1] having the formula

$$C_3H_5[O.C_{18}H_{33}O].[O.C_{18}H_{34}(SO_4H).O].[O.C_{18}H_{34}(OH)O].$$

This reaction is made use of in the manufacture of Turkey red oils (chap. xv.).

At a temperature exceeding 100° C. concentrated sulphuric acid reacts energetically with all oils and fats, hydrolysing the fats into glycerol and sulpho-compounds of the fatty acids. The latter are decomposed into sulphuric acid and fatty acids on steaming. On this reaction is based the "acid saponification" process employed in the candle industry (see chap. xv.).

Concentrated nitric acid attacks the oils and fats, acting on them violently and with copious evolution of red fumes. Hot dilute nitric acid oxidises the oils and fats gradually. *Fahrion*[2] concludes from some experiments that all glycerides of unsaturated acids when acted on with nitric acid give rise to the formation of hydroxy acids, which on further treatment with nitric acid are said to be converted into nitro-derivatives of hydroxy acids. This statement stands in need of confirmation.

On treatment with *nitrous acid* the non-drying oils become solid, or acquire the consistency of butter according to the proportion of triolein (trierucin, etc.) they contain, the triolein (trierucin, etc.) being converted into the solid isomeride trielaïdin (tribrassidin, etc.) (cp. chap. vii. p. 301). Drying oils, on the other hand, when similarly treated, remain liquid. *Lidoff*[3] states that their specific gravity increases, as also their viscosity and saponification value, whereas the iodine and the *Hehner* values decrease. All oils, after treatment with nitrous acid, contain, according to the same author, nitrogen varying in amount from 1 to 2·5 per cent. These substances may be reduced, yielding new compounds, which probably contain the NH_2 group. The free unsaturated acids yield no such compounds. These statements stand in need of confirmation.[4]

Fuming nitric acid, in presence of concentrated sulphuric acid, reacts with linseed oil and castor oil to form "nitrated" oils, the nature of which has not been investigated yet, although they have found technical application (cp. chap. xv. "Nitrated Oils").

Chlorine and *bromine* act on fats with evolution of hydrochloric and hydrobromic acids respectively, glycerides of chloro- or bromo-substitution products of the fatty acids being formed. If triglycerides of the unsaturated acids are present, chlorine and bromine are simultaneously absorbed with formation of additive products (cp. chap. vi. p. 250).

Iodine does not yield substitution products, and is but slowly absorbed when mixed with an oil or fat. The dissolving power of oils

[1] Geitel, *Journ. Soc. Chem. Ind.* 1888, 219; *Journ. f. prakt. Chemie*, 1888 [38], 218.
[2] *Zeit. f. angew. Chemie*, 1891, 74.
[3] *Journ. Chem. Soc.* 1893, Abstracts ii. 559.
[4] Cp. Lewkowitsch, *Jahrb. d. Chemie*, 6 (1896), 378.

or fats for iodine will, therefore, vary with the chemical constitution of their glycerides and also with the temperature (cp. p. 241). Hence, such statements as *Focke's*[1] that liver oils dissolve iodine to the extent of 20 per cent, and neat's foot oil even 33 per cent of iodine, must be accepted with reserve. The dissolution of iodine in fats at the ordinary temperature is assisted by the addition of a small quantity of potassium or sodium iodide. The absorption, however, takes place readily if, following *Hübl's* process (chap. vi. p. 240), an alcoholic solution of iodine and mercury bichloride is allowed to act on a dilute solution of fats. The glycerides of the unsaturated acids absorb in that case one molecule of iodine chloride for each pair of doubly linked carbon atoms, with the formation of saturated compounds. This has been proved by the actual isolation of the chloro-iodo-additive compound of oleodistearin (*Henriques* and *Künne*[2]), and of oleodimargarin (*Holde*[3]). By heating the chloro-iodo compounds with bases (chinoline) the halogens are eliminated with the regeneration of the original glycerides. This reaction has found technical application in the preparation of iodo-bromo-fats (cp. chap. xv.) for pharmaceutical purposes.

Sulphur chloride acts energetically on fats (cp. chap. vii.). This reaction finds technical application in the manufacture of vulcanised oils (cp. chap. xv.).

Sulphur has no chemical action in the cold on oils and fats. At higher temperatures, however, from 120° to 160° C., all oils assimilate sulphur, and it would appear that the sulphur is absorbed much in the same manner as oxygen is absorbed by oils. Experiments made by *Altschul*[4] have demonstrated that stearic acid is hardly acted upon by sulphur at a temperature of about 130° C., whereas oleic acid treated with 10 per cent of sulphur at 130°-150° C. absorbs the sulphur without any evolution of sulphuretted hydrogen. In a similar manner fatty oils (because containing glycerides of the unsaturated fatty acids), notably linseed oil, castor oil, rape oil, cotton seed oil, and marine animal oils, absorb sulphur at 120°-160° C. On cooling, sulphur does not separate out; on saponifying the sulphurised oils in the cold, sulphurised fatty acids are obtained, whilst very little sulphuretted hydrogen is evolved.[5] On heating the sulphurised fatty acids to 130°-200° C., however, sulphuretted hydrogen escapes in large quantities, substitution of hydrogen in the molecule of the fatty substance taking place. Sulphur is used like sulphur chloride in the manufacture of vulcanised oils.

Carbonic acid is to some extent soluble in oils, especially so under pressure. The dissolved gas escapes with effervescence at the ordinary pressure (cp. "Effervescent Fats," chap. xv.). Lard also absorbs to some extent carbonic acid, and acquires thereby a tallow-like taste.

[1] *Pharm. Zeit.* 1896, 616.
[2] *Berichte*, 1899, 387.
[3] *Ibid.* 1902, 4306.
[4] *Journ. Soc. Chem. Ind.* 1896, 282.
[5] Henriques, *Journ. Soc. Chem. Ind.* 1896, 282.

2. Waxes (Liquid and Solid)

1. Chemical Constitution of Waxes. Preparation and Properties of Pure Waxes

The most essential point of difference between fats and waxes has been already explained. The fats are the glycyl esters of the higher fatty acids, whilst the waxes proper must be considered as esters formed by the combination of mono- or dihydric alcohols with higher fatty acids. Thus cetin, or cetyl palmitate, is obtained from cetyl alcohol and palmitic acid by abstraction of water, according to the following equation—

$$C_{16}H_{33} . OH + C_{15}H_{31} . CO . OH = C_{16}H_{33} . O . CO . C_{15}H_{31} + H_2O.$$

Therefore, whilst all fats have one common basic constituent—namely, the trihydric alcohol: glycerol—the waxes are characterised by their basic constituents being monohydric and dihydric alcohols. The alcohols hitherto identified in waxes belong both to the aliphatic and aromatic series; the former being represented by alcohols of the ethane, allylic, and glycolic series, the latter by the cholesterols. Amongst the solid fatty acids, none of a lower number of carbon atoms than myristic acid has been found hitherto. The fatty acids of wool wax are remarkable for the ease with which they are converted into lactones.[1] The nature of the liquid fatty acids in waxes has not been ascertained hitherto.

The following pure "waxes" have been isolated:—

Cetyl Palmitate, Cetin, $C_{16}H_{33} . O . CO . C_{15}H_{31}$, occurs largely in spermaceti, of which it forms the chief constituent. It is prepared by repeatedly re-crystallising spermaceti from ether. Cetin forms white crystals, melting at 55° C., easily soluble in boiling alcohol, but nearly insoluble in cold alcohol. In a vacuum cetin can be distilled unchanged. When distilled under ordinary pressure, or even under a pressure of 300 to 400 mm., it is split up into palmitic acid and the hydrocarbon hexadecylene (cetene), according to the following equation—

$$C_{16}H_{33} . O . CO . C_{15}H_{31} = C_{16}H_{32}O_2 + C_{16}H_{32}.$$

Octodecyl Palmitate, $C_{18}H_{37} . O . CO . C_{15}H_{31}$. This wax forms crystals, melting at 59° C.

Ceryl Palmitate, $C_{26}H_{53} . O . CO . C_{15}H_{31}$, is the chief constituent of opium wax. It crystallises from boiling alcohol in small prisms, having the melting point 79° C. The melting substance solidifies at 76° C.

Myricyl Palmitate, Myricin, $C_{30}H_{61} . O . CO . C_{15}H_{31}$, is the chief constituent of that part of beeswax which is insoluble in alcohol. It forms feather-like crystals, melting at 72° C.

[1] Lewkowitsch, *Journ. Soc. Chem. Ind.* 1892, 132; 1896, 14.

Cetyl Stearate, $C_{16}H_{33} . O . CO . C_{17}H_{35}$, forms large scales resembling those of spermaceti. Its melting point is 55°-60° C.

Ceryl Cerotate, $C_{26}H_{51} . O . CO . C_{25}H_{51}$, occurs in Chinese wax, which consists almost exclusively of this ester. It has also been found in opium wax, and very likely occurs in wool fat. Ceryl cerotate forms snow-white, lustrous scales (from chloroform), melting at 82·5° C.

Cocceryl Coccerate, Coccerin, $C_{30}H_{60}(O . C_{31}H_{61}O_2)_2$, has been found in the wax from cochineal. It is obtained in the form of nacreous, thin laminæ (from benzene), melting point 106° C. Coccerin is nearly insoluble in cold alcohol or ether, and dissolves with great difficulty in cold benzene and glacial acetic acid.

Cholesteryl Palmitate, $C_{26}H_{43} . O . CO . C_{15}H_{31}$, occurs in blood-serum;[1] it forms snow-white plates, melting at 77°-78° C. (*Hürthle*),[1] or long needles of silky lustre, melting at 77° C. (*Herbig*).[2] It is prepared synthetically by *Berthelot's* method (cp. cholesteryl stearate) (*Hürthle*) or by passing a current of dry hydrochloric acid through a mixture of 30 grms. of cholesterol and 50 grms. of palmitic acid at a temperature of 124° C. (*Herbig*).[2]

Cholesteryl Oleate, $C_{26}H_{43} . O . CO . C_{17}H_{33}$, has been found conjointly with the palmitate in blood-serum. It crystallises in long, thin needles, melting at about 41° C., it is soluble in ether, chloroform, and benzene, but only sparingly so in alcohol; its rotatory power is $[\alpha]_D = 18° 48'$.

Cholesteryl Stearate, $C_{26}H_{43} . O . CO . C_{17}H_{35}$, has been prepared synthetically by heating one part of cholesterol with 8-10 parts of stearic acid to a temperature of 200° C. (*Berthelot*). It has been stated to occur in wool wax conjointly with isocholesteryl stearate (cp. "Wool Wax," chap. xiv.). It crystallises in small needles, melting at 65° C. This wax is nearly insoluble in alcohol, and but slightly soluble in ether.

Isocholesteryl Stearate, $C_{26}H_{43} . O . CO . C_{17}H_{35}$, has also been obtained by synthetical methods. It crystallises in fine needles, melting point 72° C., and is but very slightly soluble in boiling alcohol.

Cholesteryl Cerotate, $C_{26}H_{43} . O . CO . C_{25}H_{51}$, is prepared by passing a current of dry hydrochloric acid through a mixture of cholesterol and cerotic acid at 145° C. for 2 hours; after repeated crystallisation from petroleum ether it forms a powdery non-crystalline mass (*Herbig*).[2] It melts at 85·5° C.

Myricyl Melissate (*Melissyl melissate*), $C_{30}H_{61} . O . O . CO . C_{29}H_{59}$, occurs in gum lac (*Gascard*); it melts at 92° C. The statement made by *Kissling*,[3] that melissyl melissate occurs in tobacco, has been refuted by *Thorpe* and *Holmes*.[4] Hence *Kissling's* note as to the occurrence of this wax in hay stands in need of confirmation.

[1] Hürthle, *Journ. Chem. Soc.* 1896, Abstr. i. 485.
[2] *Zeits. f. öffentl. Chem.* 4 (1898), 227.
[3] *Chem. Zeit.* 1901, 684.
[4] *Journ. Chem. Soc.* 1901, 982.

2. Properties of Natural Waxes

With the exception of carnaüba wax and beeswax, the waxes have not been examined yet so thoroughly that general statements can be made under this head. In the case of these two waxes, however, the occurrence of hydrocarbons has been placed beyond doubt. The hydrocarbons of beeswax belong mostly to the ethane series; their melting points are somewhat high. The hydrocarbon found in carnaüba wax is very likely a member of the same series.

The liquid waxes occurring in sperm oil most probably represent compounds of unsaturated alcohols of the series $C_nH_{2n}O$, with unsaturated fatty acids.[1]

Whereas in the case of fats, the occurrence of free fatty acids must be considered as an indication of decomposition having taken place, the same cannot be said with certainty of the waxes; at any rate in the present state of our knowledge. A certain proportion of free fatty acids is characteristic of carnaüba wax, beeswax, and (natural) wool fat, whilst the liquid waxes and spermaceti are neutral in their fresh state. [Perhaps the conjecture is permissible that the occurrence of free fatty acids is due to a secondary action, if we bear in mind that in the waxes containing free fatty acids simultaneously free alcohols are present. Glycerol being so easily soluble in water, it is evident that in the case of fats the "alcohol" escapes detection.] Therefore these waxes contain notable amounts of "unsaponifiable matter" (partly due to presence of hydrocarbons).

In their physical properties the liquid and solid waxes resemble very much the fatty oils and fats. They behave similarly to solvents; and, like fats, the waxes in a liquid condition or in solution leave a *grease-spot on paper.*

It will, therefore, suffice to emphasise the points of difference. The liquid waxes are readily distinguished from fatty oils by their lower specific gravity,—from 0·875 to 0·881. On heating, the waxes do not emit the odour of acroleïn, since glycerol is absent. When distilled destructively, the esters are converted into hydrocarbons. They do not turn rancid on keeping, owing to the stability of the esters (and the stability of their fatty acids).

Although insoluble in water, the solid waxes have the property of forming emulsions with water, so much so that large quantities of water can be incorporated with them (chap. xiv.), yielding salve-like substances.

[1] Lewkowitsch, *Journ. Soc. Chem. Ind.* 1892, 135.

CHAPTER II

SAPONIFICATION OF FATS AND WAXES

THE chemical change taking place on boiling fats with strong bases, and resulting in the formation of glycerol and of salts of the higher fatty acids, has been termed "saponification." In a wider sense, however, every chemical process by which fats or waxes are resolved into their proximate constituents—glycerol and fatty acids in the case of fats, and higher alcohols and fatty acids in the case of waxes—is called saponification, even if no bases be used to effect the reaction.

The term "saponification" is almost exclusively used in practice, its synonym, "hydrolysis," being confined to papers of a scientific character. It would appear preferable to denote by the term "hydrolysis" all those reactions in which no strong bases are used, and to restrict the term "saponification" to those processes in which glycerol and soap are obtained as the ultimate products. But it is impossible to draw a sharp line of demarcation, as there exist a number of processes in which practically complete splitting up of the glycerides is brought about by an amount of bases which is far from sufficient to neutralise the fatty acids produced.

Saponification of Fats

The chemical change which fats undergo on being hydrolysed or saponified is expressed by the following equation :—

$$(1)\quad C_3H_5\begin{matrix}O.R\\O.R\\O.R\end{matrix} + 3M.OH = C_3H_5\begin{matrix}O.M\\O.M\\O.M\end{matrix} + 3R.OH,$$

where R denotes the radicle of any fatty acid, and M stands for hydrogen or a monovalent metal. (In the case of a bivalent metal equation (1) must be replaced by equation (4).)

In the light of experiments made by *Geitel*[1] and by *Lewkowitsch*[2] this equation must be considered as a summary of the following three equations :—

[1] *Journ. f. prakt. Chemie*, 1897 (55), 429.

[2] *Journ. Soc. Chem. Ind.* 1898, 1107 ; *Proceedings Chem. Soc.* 1899, 190 ; *Berichte*, 1900, 89.

$$(1a)\quad C_3H_5\begin{matrix}O.R\\O.R\\O.R\end{matrix} + M.OH = C_3H_5\begin{matrix}O.M\\O.R\\O.R\end{matrix} + R.OH,$$

$$(1b)\quad C_3H_5\begin{matrix}O.M\\O.R\\O.R\end{matrix} + M.OH = C_3H_5\begin{matrix}O.M\\O.M\\O.R\end{matrix} + R.OH,$$

$$(1c)\quad C_3H_5\begin{matrix}O.M\\O.M\\O.R\end{matrix} + M.OH = C_3H_5\begin{matrix}O.M\\O.M\\O.M\end{matrix} + R.OH,$$

expressing the fact that hydrolysis or saponification takes place in three stages, passing from the triglyceride through the diglyceride and monoglyceride to the products of complete hydrolysis or saponification.

On carrying out "hydrolysis" or "saponification" on a practical scale we cannot expect these three stages to take place consecutively in distinct succession; or in other words, we cannot expect to find that the whole mass of triglycerides is at first hydrolysed exclusively to diglycerides, as indicated by the equation (1*a*), and that the diglycerides are then broken down to monoglycerides, as shown by the equation (1*b*), and that finally the monoglycerides so formed are converted into glycerol and free fatty acids. We shall rather find that all the three phases expressed by the above three equations take place concurrently, so that at one and the same time a molecule of diglyceride may be broken down to monoglyceride and fatty acid, or a molecule of monoglyceride to glycerol and fatty acid, whilst a molecule of triglyceride is still intact, or passes through the first phase. Therefore, on bringing about very rapid hydrolysis we cannot always observe experimentally[1] the intermediate, transitory phases; but if hydrolysis or saponification be effected somewhat slowly, we may be able to find in the partially saponified mass: (1) unsaponified triglyceride, (2) diglyceride, (3) monoglyceride, (4) glycerol, and (5) free fatty acids.

This has been verified to some extent by experiments (*Geitel*[2]; *Lewkowitsch*[3]). I select from a large number of experiments I have made, the following as best demonstrating that mono- and diglycerides are formed as intermediate products in the course of saponification:—

[1] Cp. in this respect Table 7, *Berichte*, 1900, 93; also Lewkowitsch, *Berichte*, 1903, 3766.

[2] *Journ. f. prakt. Chemie*, 1897 (55), 429.

[3] *Journ. Soc. Chem. Ind.* 1898, 1107; *Proceedings Chemical Soc.* 1899, 190; *Berichte*, 1900, 89.

[TABLE

Saponification of Tallow with Caustic Soda

Partially Saponified Tallow.	Acid Value.	Acetylated Product.		
		Acetyl Value.	Hehner Value.	Saponification Value.
Sample No. 1	12·2	17·1	94·4	207·9
,, ,, 2	12·8	24·3	94·7	210·2
,, ,, 3	20·9	18·9	94·9	206·6
,, ,, 4	31·4	9·7	95·8	203·1
,, ,, 5	45·4	15·3	96·0	208·15
,, ,, 6	77·9	11·2	97·0	206·7
,, ,, 7	105·8	52·03	...	237·65
,, ,, 8	126·8	65·6	...	252·5
,, ,, 9	145·3	78·9	...	269·0
,, ,, 10	152·4	61·8	...	252·7
Fatty Acids, obtained with Alcoholic Potash, Acetylated	...	8·8	99·5	212·8

Saponification of Tallow with Lime

Partially Saponified Tallow.	Acid Value.	Acetylated Product.		
		Acetyl Value.	Hehner Value.	Saponification Value.
Sample No. 1	20·6	13·9	93·3	210·05
,, ,, 2	40·9	22·3	93·5	215·3
,, ,, 3	79·0	16·6	93·5	214·6
,, ,, 4	46·1	15·7	94·5	212·3
,, ,, 5	50·98	27·9	93·87	221·4
,, ,, 6	59·6	28·0	93·6	223·75
,, ,, 7	114·2	...	94·97	216·5
,, ,, 8	122·05	27·2	95·5	226·7
,, ,, 9	110·9	42·0	93·8	239·35
,, ,, 10	128·4	...	95·57	218·7
Fatty Acids, obtained with Alcoholic Potash, Acetylated	...	6·7	99·5	212·8

Saponification of Cotton Seed Oil with Caustic Soda

Partially Saponified Oil.	Acid Value.	Acetylated Product.		
		Acetyl Value.	Hehner Value.	Saponification Value.
Sample No. 1	1·63	14·15	...	...
,, ,, 2	3·4	25·9	...	221·7
,, ,, 3	18·4	27·3	...	226·7
,, ,, 4	39·7	21·6	...	232·85
,, ,, 5	45·3	29·8	...	222·65
,, ,, 6	57·0	29·5	...	231·4
,, ,, 7	71·8	25·0	...	225·3
,, ,, 8	95·5	20·8	...	223·8
,, ,, 9	108·2	25·85	...	235·0
,, ,, 10	113·7	22·4	...	221·2
,, ,, 11	161·0	21·7	...	219·9
Original Oil, Acetylated	...	15·8	...	...
Fatty Acids, obtained with Alcoholic Potash, Acetylated	201·2	17·9	...	...

Saponification of Cotton Seed Oil with Lime

Partially Saponified Oil.	Acid Value.	Acetylated Product.		
		Acetyl Value.	Hehner Value.	Saponification Value.
Sample No. 1	0·5	14·9	94·5	206·3
,, ,, 2	0·6	20·0	92·84	209·2
,, ,, 3	16·0	43·15	92·0	230·1
,, ,, 4	17·6	59·2	89·1	240·0
,, ,, 5	19·9	28·3	92·35	215·3
,, ,, 6	53·4	24·9	93·8	214·8
,, ,, 7	73·2	32·4	93·6	223·4
Original Oil, Acetylated	0·0	11·7	93·5	...
Fatty Acids, obtained with Alcoholic Potash, Acetylated	199·45	13·8	99·4	216·4

The occurrence of dierucin in old rape oil, for a long time looked upon as an exceptional phenomenon, is now satisfactorily explained, and the presence of mono- and diglycerides in rancid fats becomes very probable.

Since in the absence of water no hydrolysis can take place, water must be considered as the hydrolysing agent, whether it be employed alone, or whether its action be assisted by catalytic agents, such as acids or ferments. In these cases the reaction is expressed by the following equation :—

$$(2)\ C_3H_5\begin{matrix}O.R\\O.R\\O.R\end{matrix}+3H.OH=C_3H_5\begin{matrix}O.H\\O.H\\O.H\end{matrix}+3R.OH$$

If bases be chosen as catalysts, a further chemical reaction takes place, viz. the combination of the base with the fatty acids. Thus, if in equation (1) M be a monovalent metal, say sodium, the final products will be glycerol and soda soap, as expressed by the equation :—

$$(3)\ C_3H_5\begin{matrix}O.R\\O.R\\O.R\end{matrix}+3Na.OH=C_3H_5\begin{matrix}O.H\\O.H\\O.H\end{matrix}+3Na.OR$$

On a large scale the fats are decomposed by various methods. These will be considered from a technical point of view in Chapter XV. Here it must suffice to include them in a short review of processes leading to hydrolysis.

It has been pointed out already (p. 21) that at a high temperature water alone can effect hydrolysis. This reaction can be realised in practice, and has indeed been carried out on a large scale by either heating fats with water under a pressure of 15 atmospheres, which is equivalent to a temperature of 220° C., or by distilling the fats in a current of superheated steam, when the fatty acids, together with the glycerol formed, are carried over by steam.

The following table, due to *Klimont*,[1] is instructive as showing the progress of hydrolysis at pressures of 7 and 15 atmospheres respectively :—

Aqueous Saponification of Neutral Fats under Pressure

30 grms. of Oil or Fat and 500 grms. of Water.

Kind of Fat or Oil.	At a Pressure of 7 Atmospheres. Acid Values after				At a Pressure of 15 Atmospheres. Acid Values after			
	2 hrs.	4 hrs.	6 hrs.	8 hrs.	1½ hrs.	2 hrs.	4 hrs.	6 hrs.
Cocoa nut oil	0·1	0·3	0·5	0·9	78·6	90·2	123·9	185·5
Japan wax	4·8	5·3	9·4	13·1	...	12·3	32·5	46·1
Tallow	17·5	37·3	67·3	84·8	...	62·3	106·3	155·8
Pressed tallow	15·3	38·3	65·5	81·6	...	60·4	98·7	160·3
Cacao butter	12·3	24·5	45·1	62·6	...	34·5	76·1	160·5
Olive oil	15·1	32·1	53·0	71·4	...	66·5	114·5	159·5
Sesamé oil	14·3	31·1	56·2	76·0	...	61·7	108·4	153·7
Cotton seed oil	10·0	23·2	36·3	51·7	...	42·2	80·2	128·6
Linseed oil	11·4	21·1	43·3	56·1	...	38·1	78·5	130·5

[1] *Zeit. f. angew. Chemie*, 1901, 1270.

On halving the acid values we obtain roughly the extent of hydrolysis expressed in percentages; in the case of cocoa nut oil, however, the figures should be multiplied by 0·4. It has also been pointed out that hydrolysis can be accelerated and the temperature reduced if the action of water be assisted by a catalytic agent. A suitable catalyst is hydrochloric acid, which obviously does not take part in the chemical change, but merely accelerates the hydrolysis primarily brought about by water. This is illustrated by a series of experiments made by *Lewkowitsch*,[1] and detailed in the following table:—

Hydrolysis of Oils and Fats by means of Hydrochloric Acid, Sp. Gr. 1·16

100 grms. of Oil or Fat boiled with 100 c.c. of Acid.

Oil or Fat.	Original Acid Value.	Acid Value after 24 hours' Boiling.	Acid Value of completely Hydrolysed Oil or Fat.
Cotton seed	0·35	143·9	202
Whale	6·01	157·3	195
Rape	2·16	131·7	185
Lard	1·25	140·3	201
Tallow	11·15	150·0	200
Cocoa nut	18·75	204·9	260[1]
Castor	1·22	49·14	190

In these experiments a certain amount of hydrochloric acid had escaped as gas; hence, in the experiments described in the following table, a fresh amount of acid was used after each sample had been taken from the bulk:—

[1] *Journ. Soc. Chem. Ind.* 1903, 67.

[TABLE

Hydrolysis of Oils and Fats by means of Hydrochloric Acid, Sp. Gr. 1·16

100 grms. of Oil or Fat and 100 c.c. of Acid; fresh acid used after each sample had been taken.

Oil or Fat.	Original Acid Value.	Acid Values after										Acid Value of completely hydrolysed Oil or Fat.
		2 hrs.	7 hrs.	9 hrs.	12 hrs.	14 hrs.	16 hrs.	18 hrs.	20 hrs.	22 hrs.	24 hrs.	
Cotton seed .	0·35	18·42	79·6	95·51	116·2	136·4	144·9	155·7	164·8	168·2	175·8	202
Whale . .	6·01	26·69	101·3	120·3	142·7	155·4	162·3	170·0	172·0	...	...	195
Rape . .	2·16	19·66	75·06	89·57	107·2	120·1	127·3	134·2	140·3	144·0	151·8	185
Lard . .	1·25	14·51	84·78	116·8	139·8	149·4	152·1	162·7	168·0	173·0	177·0	201
Tallow . .	11·15	43·39	112·5	131·7	153·2	167·0	173·3	178·9	183·3	185·2	186·8	200
Cocoa nut .	18·75	79·73	184·2	210·5	221·4	230·8	233·4	239·8	241·1	246·1	250·1	260
Castor . .	1·22	44·4	47·3	49·0	51·4	51·4	47·9	49·2	46·8	44·4	41·64	190

The exceptional behaviour which castor oil exhibits, can only find its explanation in the different constitution of its fatty acids, and the ready formation of polymerisation products (cp. chap. i. p. 14, chap. iii. p. 118).

The following three tables describe a number of experiments which were carried out with a view to still further accelerating, if possible, the action of hydrochloric acid.

Hydrolysis of Oils and Fats by means of Hydrochloric Acid, Sp. Gr. 1·16

100 grms. of Oil or Fat, containing Free Fatty Acids, and 100 c.c. of Acid ; fresh acid used after each sample had been taken.

Oil.	Original Acid Value.	Acid Values after										
		2 hrs.	4 hrs.	7 hrs.	9 hrs.	12 hrs.	14 hrs.	16 hrs.	18 hrs.	20 hrs.	22 hrs.	24 hrs.
Cotton seed . .	10·51	37·69	71·1	88·73	94·85	103·9	113·6	117·1	119·7	125·6	132·1	140·3
Whale . . .	15·16	41·44	85·84	105·0	123·2	147·3	158·6	164·3	173·9	175·3	...	...
Rape . . .	9·17	32·1	61·31	75·36	78·09	92·55	101·4	110·1	128·9	132·6	139·6	145·2
Lard . . .	11·3	14·52	49·58	71·46	86·36	101·2	116·8	128·5	138·0	147·3	148·7	155·0
Tallow . . .	20·14	49·41	114·9	140·7	151·5	167·6	175·8	178·6	182·9	183·3	189·0	189·4
Castor . . .	10·98	46·8	50·9	46·8	47·4	47·9	48·5	48·4	46·8	43·3	47·11	48·34

Lard boiled with Hydrochloric Acid and 1 per cent of the Substances

	Original Acid Value.	Acid Values after										
		2 hrs.	4 hrs.	7 hrs.	9 hrs.	12 hrs.	14 hrs.	16 hrs.	18 hrs.	20 hrs.	22 hrs.	24 hrs.
Mercury	1·25	12·32	35·24	63·34	96·44	133·5	145·5	154·0	164·4	169·1	174·0	174·6
Copper sulphate	1·25	19·68	53·06	82·45	89·81	131·8	146·7	153·1	156·9	164·6	171·3	175·4
Mercuric oxide	1·25	29·47	66·74	88·48	129·1	149·3	156·0	160·2	167·4	178·0	178·1	182·9
Zinc	1·25	17·88	85·94	127·3	146·0	163·7	168·0	172·7	178·5	182·0	183·1	185·7
Zinc-dust	1·25	17·07	58·83	88·23	98·13	118·1	129·7	136·7	144·0	150·8	156·0	163·0
Aluminium chloride	1·25	16·88	16·91	78·65	100·7	125·4	136·8	138·9	152·7	159·4	166·7	166·8
Nitrobenzene	1·25	56·77	103·5	120·6	129·3	147·1	152·3	158·9	163·2	166·9	168·7	171·1
Aniline	1·25	18·16	19·56	86·3	96·44	119·1	131·1	134·8	135·6	142·1	150·4	152·1

Lard containing Free Fatty Acids boiled with Hydrochloric Acid and 1 per cent of the Substances

	Original Acid Value.	Acid Values after										
		2 hrs.	4 hrs.	7 hrs.	9 hrs.	12 hrs.	14 hrs.	16 hrs.	18 hrs.	20 hrs.	22 hrs.	24 hrs.
Mercury	11·3	21·64	48·82	80·0	102·2	119·4	134·0	144·0	151·3	156·4	160·4	161·6
Copper sulphate	11·3	56·91	99·97	115·0	142·0	159·9	169·0	175·6	178·7	181·1	183·4	186·2
Mercuric oxide	11·3	32·21	67·47	99·9	108·5	113·8	144·8	150·3	153·0	154·5	157·4	161·2
Zinc	11·3	42·04	74·65	86·39	117·6	134·8	146·8	155·6	158·3	165·8	169·4	174·6
Zinc-dust	11·3	16·96	33·0	56·05	72·6	88·49	100·0	106·4	109·6	118·1	123·9	134·2
Aluminium chloride	11·3	62·15	90·56	121·0	127·3	138·5	145·3	145·6	151·4	156·2	159·2	161·9
Nitrobenzene	11·3	32·45	76·74	111·0	122·3	129·9	134·0	139·0	143·6	150·0	156·3	161·9
Aniline	11·3	34·51	74·1	74·76	93·26	106·9	119·3	124·7	128·9	133·9	138·2	141·0

The numbers given in the tables show that hydrolysis becomes very much slower when about 75 per cent of the neutral fats has been hydrolysed. The fact that under the conditions of the experiments it was very difficult to keep up a thorough intermixture of fat and acidulated water, satisfactorily explains the slowing down of the reaction. It may be safely assumed that provided a thorough intermixture, as in an emulsion, could be brought about, hydrolysis would proceed much more rapidly. For the catalytic action of hydrochloric acid takes place even at the ordinary temperature in course of time, as proved by the following experiment carried out in my laboratory [1]:—

100 grms. of cotton seed oil shaken through with 50 c.c. hydrochloric acid:

Original acid value	0·35
After 1 day, Acid value	1·22
,, 7 days, ,, ,,	3·66
,, 107 ,, ,, ,,	95·10
,, 213 ,, ,, ,,	130·20

Much better results are obtained by means of *concentrated sulphuric acid*, which seems to act as an emulsifying agent in the technical process of *hydrolysis by means of concentrated sulphuric acid* (Acid saponification, sulphuric acid saponification; cp. chap. xv.). The action of sulphuric acid consists, in the first instance, in the formation of sulpho-compounds of the glycerides (p. 13). The composition of such compounds has been investigated by *Geitel*.[2] They form a complete emulsion with water, and in order to bring about hydrolysis, the product obtained by intermixing fats with concentrated sulphuric acid must be heated and agitated by steam. Experiments instituted in my laboratory [3] illustrate the progress of hydrolysis, as shown in the following table:—

Tallow hydrolysed with 4 per cent of concentrated Sulphuric Acid at 120° C.

	Contained Free Fatty Acids. Per cent.
Sample taken after 1 hour's steaming	42·1
,, ,, 2 hours' ,,	65·1
,, ,, 3 ,, ,,	79·3
,, ,, 4 ,, ,,	83·7
,, ,, 5 ,, ,,	88·6
,, ,, 6 ,, ,,	91·7
,, ,, 7 ,, ,,	91·7
,, ,, 8 ,, ,,	92·3
,, ,, 9 ,, ,,	93·0

In the following table I have collated a number of experiments (unpublished) carried out by me with a view to ascertaining the amount of hydrolysis brought about by sulphuric acid of varying strength. It will be seen that there is a gradual decrease of hydrolysis until, at the concentration of 60 per cent of SO_4H_2, the hydrolysing action ceases altogether.

[1] Unpublished results.

[2] *Journ. f. prakt. Chemie*, 1888 (37), 53. Cp. Lewkowitsch, *Journ. Soc. Chem. Ind.* 1897, 392.

[3] Unpublished results.

Hydrolysis of Tallow, containing 6·2 per cent Free Fatty Acids, with 4 per cent of Sulphuric Acid of varying strength (Lewkowitsch)

Sulphuric Acid containing per cent SO_4H_2.	Per cent Fatty Acids. After steaming for hours																					
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22
98	42·1	65·1	79·3	83·7	88·6	91·7	91·7	92·3	93·0	92·3	93·0	93·6	93·6	93·0	93·6	93·6						
90	37·2	47·7	57·6	65·1	72·5	76·0	80·0	81·8	83·6	86·2	88·0	86·8	88·6	88·6	89·0	90·5	90·5					
85	34·1	45·2	50·8	62·6	68·2	73·1	75·0	76·2	79·4	84·3	84·9	89·3	89·3	89·3	89·9	89·9	89·9					
80	31·6	45·2	57·6	65·1	73·1	75·4	79·3	80·6	83·7	85·5	87·4	88·6	89·0	89·9	89·9	89·9						
70	15·5	16·7	17·9	18·3	18·6	20·3	24·8	26·5	28·5	31·0	32·6	34·7	35·4	37·0	39·0	40·1	42·7	45·2	46·5	47·7	47·7	47·7
60	6·2	6·2	6·2	6·2																		
50	6·2	6·2	6·2	6·2	6·8																	

A similar emulsifying action is produced by means of the sulpho-aromatic compound invented by *Twitchell*.[1] The addition of about 1-2·5 per cent of this reagent will effect practically complete hydrolysis of oils and fats, if they are heated by a current of steam, especially in the presence of a few per cent of free fatty acids, which have been found to favourably influence the starting of hydrolysis. A series of experiments carried out in my laboratory gave the results set out in the following table:[2]—

[1] E.P. 4741, 1898; D.R.P. 11449. Cp. also chap. xv.
[2] Hitherto unpublished results.

[TABLE

Hydrolysis of Oils and Fats by means of Twitchell's Reagent

100 grms. of Oil or Fats, steamed up with 1 per cent of the Sulpho-aromatic Compound in open flasks.

Oil or Fat.	Original Acid Value.	Acid Value after															
		2 hrs.	7 hrs.	9 hrs.	12 hrs.	14 hrs.	16 hrs.	18 hrs.	20 hrs.	22 hrs.	24 hrs.	26 hrs.	28 hrs.	30 hrs.	32 hrs.	34 hrs.	36 hrs.
Cotton seed .	5·67	8·75	61·28	99·8	129·4	137·6	148·7	150·1	155·9	157·9	161·4	164·5	165·2	166·3	107·0	168·4	168·9
Whale . .	6·01	14·99	48·69	63·72	72·42	80·8	84·31	85·82	89·68	90·71	91·67	91·67	91·7	94·69	97·88	98·07	98·9
Rape . .	2·16	8·4	23·24	30·59	44·26	50·57	53·6	55·4	56·58	56·72	57·91	59·58	60·6	61·46	61·61	61·87	62.3
Lard . .	2·6	11·37	38·66	58·73	82·42	90·81	98·49	107·3	107·9	109·0	110·5	112·0	115·2	118·3	118·6	119·1	120·2
Tallow . .	11·15	15·08	25·68	48·44	49·39	50·11	52·03	53·1	58·85	55·6	57·11	59·82	60·23	63·95	66·2	67·3	68·5
Cocoa nut .	18·75	114·0	221·4	232·9	233·2	236·0	236·2	237·2	237·9	238·9	239·5	239·8	239·8	240·6	240·9	241·0	241·2

I have further instituted a series of experiments made with the sulpho-aromatic compounds prepared from naphthalene, anthracene, and phenanthrene. From the numbers given in the following two tables it will be seen that the reagent prepared from naphthalene is much more effective than that from anthracene or phenanthrene, but in each case hydrolysis practically reaches 100 per cent after a given time.

Hydrolysis of Cotton Seed Oil by means of 1 per cent of Sulphostearo-aromatic Compounds (Lewkowitsch)

(*a*) Neutral Oil.

Sulphostearo-aromatic Compound of	Original Acid Value.	6½ hrs.	13 hrs.	19½ hrs.	26 hrs.	32½ hrs.	39 hrs.	45½ hrs.
Naphthalene .	1·22	146·7	190·7	201·4	211·4	...	...	...
Anthracene .	1·22	2·5	21·8	76·3	170·7	186·5	190·7	...
Phenanthrene .	1·22	45·7	125·7	177·7	183·6	194·1	201·2	...

(*b*) Oil containing Free Fatty Acids.

Sulphostearo-aromatic Compound of	Original Acid Value.	6½ hrs.	13 hrs.	19½ hrs.	26 hrs.	32½ hrs.	39 hrs.	45½ hrs.
Naphthalene .	8·3	30·9	194·1	216·9	210·7	...	...	...
Anthracene .	8·3	15·01	60·5	112·4	147·2	148·2	189·8	202·8
Phenanthrene .	8·3	42·3	159·9	156·4	181·6	184·2	204·2	204·2

The important influence which complete emulsion with water has on the progress of hydrolysis is most convincingly demonstrated by the power of ferments to hydrolyse oils and fats.

Connstein, Hoyer, and *Wartenberg*[1] have shown by an extended series of experiments that the ferment contained in castor seed is capable of hydrolysing triglycerides, provided they are completely emulsified with acidulated water. From their observations I have collated the following table :—

[1] *Berichte*, 1902, 3989.

[TABLE

Hydrolysis of Oils and Fats by means of Castor Seed Ferment

Oil or Fat	Grms.	Castor Seed. Raw.	Castor Seed. Extracted.	Fatty Acids formed. Per Cent.	After Hours.	Temperature.	Acid.
		Grms.	Grms.			°C.	Grms. $^{n}/_{10}SO_4H_2$
Tallow . . .	6·5	5	...	72	19	35	4 ,, ,,
Bone fat . .	6·5	5	...	81	19	35	4 ,, ,,
Cotton seed oil .	6·5	5	...	84	19	35	4 ,, ,,
Palm oil . .	6·5	5	...	87	19	35	4 ,, ,,
Rape oil . .	6·5	5	...	84	19	35	4 ,, ,,
Palm nut oil .	16·5	5	...	76·6	20	Ordinary	8 ,, ,,
Arachis oil . .	25	...	1·3	100	96	,,	5 ,, ,,
Rape oil . .	25	...	...	100	96	,,	5 ,, ,,
Poppy seed oil .	25	...	...	100	96	,,	5 ,, ,,
Linseed oil . .	50	...	5	83	24	,,	10 ,, ,,
Blubber oil (I.) .	50	...	5	76	24	,,	10 ,, ,,
,, ,, (II.) .	50	...	5	84	24	,,	10 ,, ,,
Olive oil . .	50	...	5	86	24	,,	10 ,, ,,
Sesamé oil . .	50	...	5	85	24	,,	10 ,, ,,
Almond oil . .	50	...	5	90	24	,,	10 ,, ,,
Cacao butter . .	50	...	5	92	24	,,	10 ,, ,,
Palm oil [1] . .	75	...	7·5	77	6	,,	15 ,, ,,
,, ,, . .	75	...	7·5	96	22	,,	15 ,, ,,
Cotton seed oil .	75	...	1·5	82	44	,,	15 ,, ,,
,, ,, .	100	...	5	87	44	,,	10 ,, ,,
,, ,, .	75	...	7·5	79	24	,,	15 ,, ,,
Triolein . .	10	...	...	50·6	24		
Triacetin . .	10	...	0·5	0·4	24		2 ,, ,,
Tributyrin . .	10	...	...	9·5	24		

The last two lines show that whereas the glycerides of the higher fatty acids are comparatively easily hydrolysed, the glycerides of the lower fatty acids offer much greater resistance.

The extent of hydrolysis stands in a definite proportion to the amount of ferment present, as shown by the following numbers:—

[1] The percentages of free fatty acids in the original palm oil were not stated.

[TABLE

Hydrolysis of Castor Oil by means of Castor Seed Ferment, showing the Influence of the Quantity of Seed

	Grms.	Extracted Castor Seed.	Fatty Acids formed. Per cent.	After Hours.	Acid.
		Grms.			
Castor oil	5	0·5	89	24	5 grms. 2 per cent acetic acid
			92	48	
,, ,,	10	0·5	81	24	10 ,, ,,
			86	48	
,, ,,	15	0·5	77	24	15 ,, ,,
			87	48	
,, ,,	20	0·5	71	24	20 ,, ,,
			80	48	
,, ,,	25	0·5	60	24	25 ,, ,,
			74	48	
,, ,,	50	0·5	49	24	50 ,, ,,
			49	48	
,, ,,	10	0·2	55	24	10 ,, ,,
			64	48	10 ,, ,,
			70	72	10 ,, ,,
			70	96	10 ,, ,,
			78	120	10 ,, ,,
			79	144	10 ,, ,,
			79	168	10 ,, ,,
			79	240	10 ,, ,,

The quantity of water emulsified with the fats also influences favourably the amount of hydrolysis up to a certain extent, as will be gathered from the following table :—

Hydrolysis of Castor Oil by means of Castor Seed Ferment, showing the Influence of the Quantity of Water

	Grms.	Castor Seed containing Oil.	Free Acids formed. Per cent.	After Hours.	Acid.
		Grms.			
Castor oil	6·5	5	68	3	2 grms. 2 per cent acetic acid
			74	18	
			74	42	
,, ,,	6·5	5	74	3	4 ,, ,,
			80	18	
			84	42	
,, ,,	6·5	5	75	3	6 ,, ,,
			84	18	
			80	42	
,, ,,	6·5	5	76	3	8 ,, ,,
			87	18	
			85	42	
,, ,,	6·5	5	76	3	10 ,, ,,
			86	18	
			86	42	

Not all ferments exhibit the power of hydrolysing glycerides in so pronounced a manner. Thus, whilst lipase—a ferment contained in the liver—hydrolyses ethyl butyrate somewhat readily,[1] it hardly attacks oils and fats, as I have shown recently.[2]

On the other hand, steapsin, the ferment contained in the pancreas, is a comparatively powerful fat-hydrolysing ferment, as I have proved in collaboration with *Macleod*.[3] The following table recapitulates some of the results obtained with two steapsin preparations "1" and "2":—

[1] Kastle and Loevenhart, *Journ. Amer. Chem. Soc.* 1900 (24), 49.
[2] *Journ. Soc. Chem. Ind.* 1903, 78.
[3] *Proc. Royal Society*, 1903 (72), 31.

[TABLE

Hydrolysis with the aid of Steapsin Preparations

Preparation.	Cubic Centimetres of Preparation per 100 Grms. of Cotton Seed Oil or Lard.	Date on which started.	Added to Emulsion.		Percentage of Free Fatty Acids formed.					
			Acid.	Alkali.	Feb. 23.	Mar. 2.	Mar. 9.	Mar. 16.	Apr. 16.	May 1.
	Cotton Seed Oil.									
1	20	19/2/03	0	0	22·9	...	43·3	48·4	80·6	...
1	30	19/2/03	0	0	32·8	...	49·9	60·45	86·7	...
1	25	19/2/03	0·5 c.c. of 2 per cent acetic acid	0	10·22	26·4	41·04	48·8	74·7	...
1	30	19/2/03	0	0·5 c.c. 1/10 norm. NaOH	31·25	39·5	55·4	63·1	...	...
2	30	5/3/03	0	0	...	...	37·1	44·3	68·3	70·2
2	50	5/3/03	0	0	...	...	32·7	46·4	71·5	83·8
2	60	5/3/03	0	0	...	...	31·03	46·3	60·8	79·5
2	60	5/3/03	0·5 c.c. of 2 per cent acetic acid	0	...	...	30·4	45·2	65·3	73·7
2	60	5/3/03	0	0·5 c.c. 1/10 norm. NaOH	...	...	36·5	44·9	66·4	73·5
2	30	5/3/03	0	1 c.c. 1/10 norm. NaOH	...	...	31·4	43·8	74·1	74·3
2	50	5/3/03	1 c.c. of 2 per cent acetic acid	0	...	...	37·66	44·5	65·2	77·2
	Lard.									
2	50	5/3/03	0	0·5 c.c. 1/10 norm. NaOH	...	...	8·98	9·2	29·9	16·7
2	80	5/3/03	0	1 c.c. 1/10 norm. NaOH	...	...	12·2	14·4	20·7	22·9

Another class of accelerating agents, employed on a very large scale, are basic materials, such as zinc oxide, magnesium oxide, calcium oxide, and in a very prominent manner the caustic alkalis.

Now, if the view that the bases act as accelerating agents, in other words as catalysts, be correct, then it should not be imperative that the bases be present in at least molecular proportion to the fatty acids that will result on complete hydrolysis. The greater the amount of the bases present, the more rapidly should the resolution of the glycerides into their components take place, and the greater the amount of salts of the fatty acids; but a deficiency of the bases to neutralise all the fatty acids obtainable by complete hydrolysis, should not preclude the completion of hydrolysis.

Since the rapidity of saponification stands in direct ratio to the quantity of the bases, it will be possible in presence of an excess of bases to lower the temperature required for effecting hydrolysis, and to shorten the time in which it reaches practical completion. These points are clearly brought out in the technical process of saponification by means of lime. The quantity of lime required to neutralise the fatty acids produced on completely hydrolysing a glyceride can be calculated from the following summarising equation :—

$$(4)\quad 2C_3H_5\begin{matrix}OR\\OR\\OR\end{matrix} + 3Ca(OH)_2 = 2C_3H_5\begin{matrix}OH\\OH\\OH\end{matrix} + 3Ca(OR)_2.$$

The amount of caustic lime—CaO—required for a triglyceride having the mean molecular weight 860, is 9·7 per cent, but even prolonged boiling with steam in an open vessel with that amount of lime will not lead to complete saponification. Unless the proportion of caustic lime be raised to 12-14 per cent, the hydrolysis of the glyceride cannot be brought to an end in an open vessel, *i.e.* at a temperature of from 100°-105° C. If, however, the temperature be raised (as is done on a large scale by treating the fats with milk of lime in an autoclave under pressure), the proportion of caustic lime can be reduced gradually until, at a pressure of 12 atmospheres, corresponding to a temperature of 220° C., even 1 per cent of lime suffices for practically complete hydrolysis. Although the glyceride is completely hydrolysed, only so much of the fatty acid is neutralised by lime, *i.e.* converted into lime soap, as is chemically equivalent to the quantity of lime.

The same considerations—*mutatis mutandis*—hold good if magnesium oxide or caustic alkalis are used as accelerators. In the last case, hydrolysis proceeds much more rapidly, inasmuch as in contradistinction to hydrolysis assisted by lime, a water-soluble soap is formed, which helps to emulsify the fats. There can be no doubt that under pressure complete hydrolysis would be brought about by an amount of caustic alkali insufficient to neutralise all the fatty acids formed. On a large scale, for tolerably obvious reasons, such a process is not employed. The compounds resulting from the combination of fatty acids and caustic alkalis being useful com-

mercial products, the aim of the manufacturer is to so conduct operations that these products—soaps—are obtained concurrently with the hydrolysis of the fats. Hence, on a commercial scale the oils and fats are boiled in open vessels with a solution of caustic alkali, which is not only sufficient to neutralise all the fatty acids obtainable on hydrolysing the glycerides, but provides also an excess of alkali in order to shorten the time required for the completion of the reaction. This excess of alkali is required in order to carry out the reaction in a limited time.

For in consonance with the law of mass action, the velocity of the reaction will be great at the beginning and will gradually slow down until an equilibrium is established between the tendency of alkali to neutralise the acids on the one hand, and the opposite tendency of water to dissociate the soap formed on the other. Hence, under the given conditions of temperature and pressure, an equilibrium will be established very rapidly, beyond which no further progress will occur.

This is clearly brought out by the following experiment carried out in my laboratory by *Clapham*:—

2000 grms. of tallow were boiled by means of open steam, as in the method employed on a large scale, with 282 grms. of pure caustic soda,—the theoretical quantity required to neutralise the fatty acids obtainable. The boiling was continued beyond the time required on a manufacturing scale. The pasty soap was then examined with the following result:—

	Per cent.
Total fatty matter	33·00
Total alkali	3·708
Fatty acids as soap	31·01
Combined alkali as soap	3·496
Unsaponified fat	2·0
Free alkali	0·212

This experiment shows that only 94 per cent of tallow were saponified. On adding an excess of alkali, the equilibrium between the reacting masses is changed in the direction of a greater amount of soap being formed, so that by employing a suitable excess—as is done on a large scale—complete hydrolysis of the fat, followed immediately by complete neutralisation of the fatty acids, is obtained.

From the foregoing it will be evident that for *analytical* purposes the most rapid method to hydrolyse fats consists in using caustic alkalis. Since, however, even the employment of an excess of alkali in aqueous solution entails a very lengthy operation, which is not always carried out successfully by an analytical chemist without some little practical experience in soap-making, it is necessary to still further accelerate hydrolysis in the laboratory. This is done by employing caustic alkalis in strong ethylalcoholic (or amylalcoholic) solution.

The action of caustic soda in alcoholic solution need not be considered as differing theoretically from hydrolysis in aqueous solution, if we look upon alcohol as water in which one hydrogen atom is re-

placed by the group C_2H_5 (or C_5H_{11}). Ignoring for a moment the alkali, the reaction would then proceed according to the following equation :—

$$\text{(5)}\ C_3H_5\overset{OR}{\underset{OR}{OR}} + 3H\,.\,OC_2H_5 = C_3H_5\overset{OH}{\underset{OH}{OH}} + 3R\,.\,OC_2H_5.$$

which should again be taken as the summary of the following three equations :—

$$\text{(5a)}\ C_3H_5\overset{OR}{\underset{OR}{OR}} + H\,.\,OC_2H_5 = C_3H_5\overset{OH}{\underset{OR}{OR}} + R\,.\,OC_2H_5,$$

$$\text{(5b)}\ C_3H_5\overset{OH}{\underset{OR}{OR}} + H\,.\,OC_2H_5 = C_3H_5\overset{OH}{\underset{OR}{OH}} + R\,.\,OC_2H_5,$$

$$\text{(5c)}\ C_3H_5\overset{OH}{\underset{OR}{OH}} + H\,.\,OC_2H_5 = C_3H_5\overset{OH}{\underset{OH}{OH}} + R\,.\,OC_2H_5.$$

The resulting products would be glycerol and the ethylic esters of the fatty acids. The feasibility of these reactions has not yet been tested experimentally, but with anhydrous materials and under high pressure, especially if assisted by a suitable catalyst,[1] it is very likely the reaction will proceed a long way in the direction indicated by the equation (5).

In the absence of water the reaction cannot proceed beyond the formation of ethyl esters. But if the alcohol contain water, the ethylic esters in their turn are hydrolysed to some extent by the water. Yet complete hydrolysis, as indicated by the following equation :—

$$\text{(6)}\ 3C_2H_5\,.\,O\,.\,R + 3H\,.\,OH = 3R\,.\,OH + 3C_2H_5\,.\,OH,$$

cannot result, since an equilibrium between ester, water, and free fatty acids would soon be established. The reaction thus arrested *will, however, proceed if alkali is present to neutralise the free acid* formed. Since in laboratory operations caustic alkali is added to the alcohol in a quantity greater than that which is chemically equivalent to the fatty acids, the fatty acids formed (equation (6)) will be immediately neutralised as shown in equation :—

$$\text{(7)}\ 3R\,.\,OH + 3Na\,.\,OH = 3Na\,.\,OR + 3H\,.\,OH,$$

so that the reaction represented by equation (6) will become completed. By adding the three equations (5), (6), and (7)

$$\text{(5)}\ C_3H_5\overset{OR}{\underset{OR}{OR}} + 3H\,.\,OC_2H_5 = C_3H_5\overset{OH}{\underset{OH}{OH}} + 3RO\,.\,C_2H_5,$$

$$\text{(6)}\ 3R\,.\,OC_2H_5 + 3H\,.\,OH = 3R\,.\,OH + 3H\,.\,OC_2H_5,$$

$$\text{(7)}\ 3R\,.\,OH + 3Na\,.\,OH = 3Na\,.\,OR + 3H\,.\,OH,$$

---

[1] Cp. Lewkowitsch, "Problems in the Fat Industry," *Journ. Soc. Chem. Ind.* 1903, 595.

we obtain as the final result :—

$$C_3H_5\begin{matrix}OR\\OR\\OR\end{matrix} + 3NaOH = C_3H_5\begin{matrix}OH\\OH\\OH\end{matrix} + 3NaOR,$$

which is identical with the above given equation (3).

The correctness of the views I have given here is confirmed by a number of observations. Thus *Duffy* has shown that on boiling tristearin with a solution of sodium in absolute alcohol, it is partially converted into ethyl stearate. *Bouis* also demonstrated the formation of ethyl stearate by heating tristearin, dissolved in ether, with small quantities of alcoholic potash, and further showed that all the glycerol was split off, the chemical change taking place in the course of one or two minutes. *J. Bell* found that on boiling butter fat with half the quantity of alcoholic potash required for complete saponification, a light oil is obtained, solidifying at 43° C. This oil, looked upon by him as a diglyceride of the composition $C_3H_5(OH)(OC_{16}H_{31}O)(OC_{18}H_{33}O)$, was actually a mixture of ethyl esters of fatty acids. *Allen*[1] ascertained similarly that on heating acetin with the fiftieth part of alcoholic potash required for complete saponification, 39 per cent out of the theoretically possible quantity of ethyl acetate had been formed, whilst three-fiftieth parts of potash converted 85 per cent into acetic ether. A larger proportion of alkali diminished the yield of acetic ether; thus with sufficient caustic soda to saponify 39·8 per cent of the acetin used, the amount converted into acetic acid was 52·4 per cent. The formation of ethylic esters was further demonstrated by *Kossel* and *Krüger*[2] on saponifying mutton tallow with sodium alcoholate. *Henriques*[3] confirmed the foregoing experiments by again demonstrating that if an insufficient amount of alkali be used, the chemical change taking place consists in the complete splitting off of glycerol with formation of ethylic esters (or methylic, or amylic esters, if methyl-alcohol or amyl-alcohol was substituted for ethyl alcohol). Thus he has shown that in the case of linseed, rape, almond, olive, and castor oils, the complete conversion of the glycerides into ethylic esters took place when only 33·3 or 25 or 15 per cent of the theoretical amounts of alkali was employed; in the case of castor oil, even 10 per cent was found to be sufficient.

The foregoing views rest on the fundamental principle that water is the true hydrolysing agent, and that in the absence of water the reaction cannot proceed to the formation of glycerol. Since for the hydrolysis of 1 grm. of fat no more than 0·06 grms. of water are required, the difficulty of keeping out traces of water from alcohol, especially whilst it is being boiled with the fat under examination, satisfactorily disposes of a number of experiments purporting to show that saponification will take place in the absence of water. Such experiments were first carried out with sodium alcoholate (sodium ethoxide, C_2H_5ONa) by *Bouis*.[4] Later on *Kossel* and *Obermüller*[5]

[1] *Chem. News*, 1891, 64, 179.
[2] *Zeit. f. physiol. Chemie*, 1891 (15), 321.
[3] *Journ. Soc. Chem. Ind.* 1898, 673, 853; *Zeit. f. angew. Chemie*, 1898, 697.
[4] *Compt. rend.* 45, 35.
[5] *Zeit. f. physiolog. Chemie*, 15, 321-330.

suggested the same method, as the quickest and surest means of saponifying fats completely in the laboratory, and *Kossel* and *Krüger*[1] stated that in a number of experiments with sodium ethoxide, saponification was complete if the theoretical quantity of sodium was employed. Since the reaction must take place according to the following equation :—

$$(8)\quad C_3H_5\begin{matrix}OR\\OR\\OR\end{matrix} + 3C_2H_5ONa = C_3H_5(ONa)_3 + 3ROC_2H_5,$$

it is difficult to see how glycerol can be formed in the absence of water. The difficulty has later on been removed by the statement of their collaborator *Obermüller*, that in the foregoing experiments small quantities of water had by no means been excluded, so that the sodium glyceroxide obtained according to the above equation was readily decomposed by water, with the formation of glycerol and sodium hydrate. The sodium hydrate had then only to deal with the more readily saponifiable ethylic esters, and their saponification was rapidly completed on boiling. He further showed in experiments which were carried out with carefully dried alcohol, whilst moisture from the atmosphere was excluded by means of calcium chloride during the saponification test, that about 30 per cent of the fat remained unsaponified. Considering the extreme difficulty of excluding the last traces of moisture (calcium chloride is incapable of effecting this completely) the conditions of even these experiments do not preclude the assumption that unavoidable traces of moisture effected the saponification of two-thirds of the fat.

The complete saponification by means of sodium ethoxide resulting in the production of glycerol and sodium salts of fatty acids must therefore be expressed by the following three equations :—

$$(9)\quad C_3H_5O\begin{matrix}O.R\\.R\\O.R\end{matrix} + 3C_2H_5O.Na = C_3H_5O\begin{matrix}O.Na\\.Na\\O.Na\end{matrix} + 3RO.C_2H_5,$$

$$(10)\quad C_3H_5O\begin{matrix}O.Na\\.Na\\O.Na\end{matrix} + 3H.OH = C_3H_5\begin{matrix}OH\\OH\\OH\end{matrix} + 3Na.OH,$$

$$(11)\quad 3R.OC_2H_5 + 3Na.OH = 3H.OC_2H_5 + 3Na.OR.$$

These three equations, then, represent three consecutive chemical changes, each of which in its turn must be considered as a summary of three reactions such as are represented by equations (1*a*), (1*b*), and (1*c*), and equations (5*a*), (5*b*), and (5*c*).

Although for many purposes, especially for the subsequent estimation of glycerol, it would be more convenient to use in the laboratory such bases for saponification as form insoluble salts with the fatty acids, for instance, lead oxide, lime, and baryta, they must be excluded, as saponification by means of these bases is not complete. Therefore in all analytical operations, if reliable results are to be obtained, caustic alkalis must be employed. Caustic potash is prefer-

[1] *Zeit. f. physiolog. Chem.* 1891, 15, 322.

able to caustic soda, since the potash soaps are more readily soluble than the soda soaps, and thus a more intimate contact of the reacting masses helps to bring the saponification more rapidly to an end. Although the theoretical amount required for 1 grm. of fat is from 0·19 to 0·26 grms. of caustic potash, a considerable excess is necessary to ensure satisfactory results in the shortest time.

The following are convenient proportions for saponifying fats: To 10 parts weighed in a flask are added 30 to 40 parts of alcohol[1] by volume, and 4 to 6 parts of solid caustic potash previously dissolved in 20 parts of water. The flask is then connected with an inverted condenser, and the contents are kept gently boiling for half an hour or an hour. These proportions may be varied within very wide limits. Thus *Yssel de Schepper* and *Geitel* recommend 20 grms. of fat, 40 c.c. of caustic potash of specific gravity 1·4, and 40 c.c. of alcohol, whilst *Dalican* proposes to pour into 50 grms. of fat, heated to 200° C., shaking constantly, a mixture of 40 c.c. caustic soda, specific gravity 1·33, and 33 c.c. of 95 per cent alcohol.

As commercial alcohol is seldom free from traces of acid, it should be tested, and if necessary, it must be neutralised with decinormal

[1] If the cost of spirits of wine preclude its use, recourse may be had to methylated spirit. This alcohol can be purified for analytical purposes by the following method, proposed by *Waller* (*Journ. Amer. Chem. Soc.* 1889, 124; *Analyst*, 1890, 50). The alcohol is shaken with powdered potassium permanganate until it assumes a distinct colouration. It is allowed to stand for some hours until the permanganate has been decomposed and hydrated manganese peroxide is deposited. A pinch of calcium carbonate is then added, and the alcohol distilled from a flask provided with a *Wurtz* tube or a *Le Bel-Henninger* fractionating column at a rate of about 50 c.c. in 20 minutes. The distillate is tested frequently until 10 c.c. of it, when boiled with 1 c.c. of a strong (syrupy) solution of caustic potash, gives no yellow colouration on standing for 20 or 30 minutes. What distils after that is preserved for use; care, however, has to be taken not to distil to dryness. The alcohol thus prepared is completely neutral, and is especially suitable for the preparation of alcoholic potash solution; even on standing for a long time alcoholic potash made from such alcohol does not become discoloured.

It should be noted that alcohol is methylated at present (General Order as to Methylated Spirit, July 20, 1891) by mixing with it mineral naphtha of a specific gravity of not less than 0·800. The admixed hydrocarbons are not got rid of by the foregoing processes of purification, but will pass over into the distillate with the alcohol. In estimations of "unsaponifiable" matter in fats this source of error must be specially guarded against.

Another method has been recommended by *J. Carter Bell* (*Journ. Soc. Chem. Ind.* 1893, 236), and is carried out as follows: 500 c.c. of methylated alcohol, about 85 or 90 per cent, are placed in a flask of about 1000 c.c. capacity, containing 25 grms. of stick potash. When the latter has been dissolved, 250 grms. of melted lard, or of some other saponifiable fat, are added. The flask is then connected with an inverted condenser and heated on the water-bath, when the fat is readily saponified, especially if the flask be shaken repeatedly. After the condenser has been inverted, about 450 c.c. of alcohol are distilled off. According to *Carter Bell*, the alcohol thus obtained will not turn brown on the addition of potash after several days, and when the solution is kept in a strong light only a slight yellow colour may be developed. This property of soap, to retain the impurities of methylated spirit, is well known to manufacturers of transparent soap from stock soaps by dissolving them in boiling methylated spirit. The commercial methylated spirit when *first* used for this process yields a distillate which has a much less unpleasant smell than the crude spirit. At each subsequent time of using the methylated spirit a further improvement of the quality of the alcohol takes place; ultimately a spirit is obtained which is quite free from the rank odour of the commercial article.—*Kadel* (*Pharm. Journ. and Transactions*, 1894, 356) distils impure alcohol first over caustic soda—30 grms. for 5 litres—after allowing to stand for a few days. The distillate is next treated with permanganate and distilled off again. If necessary the latter operation is repeated and followed by filtration over charcoal.

caustic alkali, using phenolphthalein as an indicator, or it may be distilled over lime or baryta immediately before use. For the purposes of fat analysis, rectified spirits of wine will, as a rule, be pure enough. It should be tested by boiling a few c.c. with several drops of concentrated caustic potash; pure alcohol will not become brown; a slight yellow colour may, however, be allowed to pass. The appearance of a brown colour would point to the presence of aldehyde or acetone.

In order to accelerate the process of saponification, *Yssel de Schepper* and *Geitel*[1] add some ether, thus ensuring a readier contact of the particles of fat and alkali. This proposal has also been made by *Hehner*,[2] *Duclaux*, and others; but I do not recommend it, as the presence of ether necessarily demands a lower temperature than would be required in many cases. *Henriques*[3] dissolves the fat in petroleum ether and mixes the solution with alcoholic soda; on standing for 12 hours, complete saponification takes place. Besides having the disadvantage that an operation which can be easily finished in half an hour is unduly protracted, this method has the further drawback that the solution of alkali must be prepared with strongest alcohol, as it is essential to obtain a homogeneous liquid on mixing the alcoholic soda with petroleum ether. Not only for these reasons, but chiefly because the sodium soaps are much less soluble than potassium soaps, so that, *e.g.*, this method cannot be recommended as one to replace the usual method. In the case of sulphurised (vulcanised) oils and fats, however, the cold saponification process may be used with advantage, as sulphur is eliminated from the fatty substance by boiling alcoholic potash to a far greater extent than when working in the cold.

The various triglycerides are not saponified with equal facility. A few of the older observations referred to the glycerides of the higher fatty acids only. Thus it has been stated that olein is hydrolysed with greater difficulty than palmitin or stearin. This statement has even led to patenting a process for obtaining olein from olive oil, which consists essentially of olein and palmitin, by shaking the oil with caustic soda in the cold, when palmitin is said to be saponified, whereas olein remains unchanged. It has, however, been shown by *Thum*[4] that there is no marked difference between oleic and commercial stearic acids in their behaviour with caustic alkalis. On adding to a mixture of oleic and commercial stearic acids an amount of caustic potash insufficient to completely neutralise the acids, the composition of the acids that had been converted into soaps was found to be almost the same as that of the acids that had remained free. Hence it is impossible to effect a separation of solid fatty acids from liquid ones by partial saturation

[1] *Dingl. Polyt. Journ.* 245, 295.

[2] *The Analyst*, 1893.

[3] *Journ. Soc. Chem. Ind.* 1896, 299, 476. The objections raised by *Henriques* to the usual method of saponification are groundless (cp. Holde, *Journ. Soc. Chem. Ind.* 1896, 476.

[4] *Journ. Soc. Chem. Ind.* 1891, 70; *Zeit. angew. Chem.* 1890, 482.

with alkali. Conversely, *Henriques*[1] has proved that on saponifying glycerides with amounts of caustic alkali, insufficient to neutralise all the fatty acids formed, no differentiation of the several esters could be observed. However, inasmuch as saponification took place somewhat rapidly in these cases, the conclusions must be accepted with reserve. The subject has not yet been so completely investigated as it deserves, and it will only be possible to arrive at definite conclusions if hydrolysis is brought about very slowly. Hydrolysis by means of ferments offers a suitable method. *Connstein, Hoyer*, and *Wartenberg* have shown in their experiments with the castor seed ferment that there is a remarkable difference in the behaviour of the glycerides. Whereas the glycerides which most frequently occur in the natural oils and fats, namely, tripalmitin, tristearin, triolein, and triricinolein, are hydrolysed with comparative ease, the glycerides of the lower fatty acids offer considerable resistance to hydrolysis. Thus tributyrin was hydrolysed to the extent of 10 per cent only, whereas triacetin was hardly hydrolysed at all. The inference that the higher glycerides occurring in the natural oils and fats are more readily hydrolysed than those of the lower fatty acids is further supported by the behaviour of the esters of monovalent alcohols, such as ethyl acetate, amyl acetate. These undergo a very small amount of hydrolysis only, as is indicated by the following table, due to *Connstein, Hoyer*, and *Wartenberg*:—

Hydrolysis of Monovalent Esters by means of the Castor Seed Ferment

	Castor Seed. Grms.	Castor Seed. Extracted.	Fatty Acids formed. Per cent.	Hours.	Acid.
Ethylacetate	5	0·5	0·25	24	5 grms. 2 % acetic acid.
			0·40	48	
			0·45	72	
Isobutylacetate	5	0·5	0·6	24	,,
			0·7	48	
			0·7	72	
Amylacetate	5	0·5	0·1	24	,,
			0·25	48	
			0·35	72	
Ethylsulphate	5	0·5	1·6	24	,,
			2·7	48	
			3·55	72	
Amylnitrate	5	...	0·7	24	,,
			0·8	48	
			0·8	72	
Benzoylbenzoate	5	...	0·65	24	,,
			0·75	48	
			0·8	72	

This behaviour is all the more remarkable as, under the influence of other hydrolysing agents such as hydrochloric acid, the glycerides

[1] *Journ. Soc. Chem. Ind.* 1898, 673, 858; *Zeit. angew. Chem.* 1898, 338, 697.

of the lower fatty acids are much more easily hydrolysed. Again, lipase hydrolyses the glycerides of the higher fatty acids with great difficulty only, whereas it attacks the simple esters somewhat easily. Finally, the above detailed experiments with steapsin show that cotton seed oil is much more easily hydrolysed than lard.

V. Meyer's rule:—Esters that are formed readily are easily saponified, and *vice versa*, does not therefore hold good under all conditions. Those fats which are not saponified readily are best heated with the alcoholic potash under pressure. I use for these purposes a copper bottle with a screwed stopper; the bottle may be immersed in water, and is not liable to breakage as seltzer-water bottles are.

The *carbonates* of the alkalis do not saponify the fats under the same conditions as do the caustic alkalis.[1] From equation (7), it would appear likely that also the carbonates may effect complete saponification under pressure with evolution of carbon dioxide.

Saponification of Waxes

In the case of waxes we have to deal with simple esters; hence saponification in stages cannot take place. By saponifying **waxes** with alkali the salts of fatty acids and higher alcohols are obtained. Thus, myricin is resolved into palmitate and myricyl alcohol, according to the following equation:—

$$C_{15}H_{31}CO.O.C_{30}H_{61} + KOH = C_{15}H_{31}CO.OK + C_{30}H_{61}.OH.$$

On diluting the alcoholic solution of a saponified wax with water, the higher alcohols, being insoluble in water, separate out and rise to the surface of the liquid, or remain suspended in it, causing turbidity of the liquid. They are separated from the soap by shaking with ether, or by evaporating the solution together with the precipitate to dryness, and exhausting with petroleum ether (cp. chap. ix. "Unsaponifiable Matter"). In practice these substances, being insoluble in water and alkalis, are termed "unsaponifiable."

The saponification of some of the waxes, as Chinese wax and especially wool wax, is effected with great difficulty under the conditions stated above for oils and fats. Wool wax must be boiled with an excess of alcoholic potash for at least twenty hours. It is, however, easily saponified by means of sodium in a solution of absolute alcohol (*Kossel* and *Obermüller's* method). The reagent is prepared by dissolving 5 grms. of metallic sodium in 100 c.c. of absolute alcohol; it must be made afresh for each series of experiments. I have shown[2] that equally satisfactory results are

[1] *M. Doyon* and *A. Morel's* statement (*Compt. rend. Soc. Biolog.* 1902 (54), 1524), that sodium carbonate, even in dilute solution effects saponification at body temperature, requires confirmation.

[2] *Journ. Soc. Chem. Ind.* 1892, 137.

obtained by saponifying with double normal alcoholic potash under pressure.[1]

The difficulty met with in the saponification of waxes is no doubt due to the fact that the soaps formed are less readily soluble than those obtained on saponifying fats. Thus in the case of wool wax,[2] *Lewkowitsch* has shown that the soaps are very sparingly soluble in water. Such soaps would naturally envelop unsaponified wax and thus protect it from contact with alkali. Therefore petroleum ether, suggested in *Henriques'* method of cold saponification, ensuring, as it does, a readier contact of alkali and wax, accelerates the reaction, especially so when the solution is heated.

[1] *Henriques'* statement that under these conditions the alkali acts on the alcohols contained in the wool fat, is unfounded. *Henriques'* objections to the usual methods of saponification are also groundless (cp. Holde, *Journ. Soc. Chem. Ind.* 1896, 476).

[2] *Fahrion* states that wool grease (the proportion of free fatty acids not being recorded) may be completely saponified on a water-bath in an open capsule by means of double normal alcoholic soda. The soap solution must be stirred constantly, evaporated down to dryness, and *repeatedly* taken up with strong alcohol, to drive off the last traces of water, then again boiled down to dryness, and kept for some time on the water-bath. This is evidently not a very expeditious process (*Zeit. angew. Chem.* 1898, 268).

CHAPTER III

CONSTITUENTS OF FATS AND WAXES

In the laboratory the fats and waxes are resolved into their proximate constituents, viz., into fatty acids and glycerol on the one hand, and into fatty acids and alcohols on the other, by saponifying with alcoholic potash solution.

The method for preparing the fatty acids of oils and fats may be described here once for all in full:—

A sufficient quantity of fat is saponified according to one of the directions already described, say by boiling 50 grms. with 40 c.c. of caustic potash solution, specific gravity 1·4, and 40 c.c. of alcohol in a porcelain dish on a water-bath with constant stirring until the soap becomes pasty. The soap is then dissolved in 1000 c.c. of water, and the solution boiled to evaporate off the alcohol; this can be effected readily by replacing the water as it boils away. Next the soap is decomposed by means of dilute sulphuric acid. When by continued boiling the fatty acids have been obtained as a clear oily layer, free from solid particles floating on the aqueous liquid, the latter is drawn off by means of a syphon, and the fatty acids washed several times with hot distilled water until all the mineral acid has been removed. Since the fatty acids of lower molecular weight dissolve in hot water, and may redden litmus paper, methylorange should be used (p. 73) to test for the complete removal of the mineral acid. The dish containing the fatty acids is then placed on a water-bath, and warmed until the fatty acids are completely liquefied. The water and impurities will settle out and the warm acids may then be poured through a dry plaited filter fitted in a hot-water funnel. The fatty acids will thus be obtained sufficiently dry for examination. If the fatty acids solidify at the ordinary temperature, it is advisable to allow the fatty layer to solidify, then to perforate the cake by means of a glass rod, pour off the acid liquid, and wash with hot water as before.

In order to test for any undecomposed fat, a sample, say about 2 c.c., is dissolved in 15 c.c. of alcohol, and 15 c.c. of aqueous ammonia are added. If an appreciable amount of fat has escaped saponification the mixture will become turbid (*Geitel*). It should, of course, be remembered that, in case the fat contain considerable quantities of unsaponifiable matter, turbidity will set in.

The acid water and wash waters contain all the glycerol originally combined with the fatty acids in the oil or fat.

If a wax be saponified in the same manner, it should be noted that the fatty layer obtained as described above, contains both the fatty acids and alcohols, and such amounts of hydrocarbons as naturally occur in the wax, whereas the wash waters contain no glycerol. In order to obtain the free fatty acids themselves, special methods must be resorted to, which will be described in Chapter VI.

The mixed fatty acids, or in the case of waxes the mixed acids and alcohols, are then resolved by scientific methods which will be detailed later on, into the individual constituents.

In this manner the following acids and alcohols have been isolated from fats and waxes :—

A. Acids

I. Acids of the series $C_nH_{2n}O_2$. Acids of the Acetic Series.

$C_2H_4O_2$	Acetic acid	$C_{17}H_{34}O_2$	Daturic acid
$C_4H_8O_2$	Buytric acid	$C_{18}H_{36}O_2$	Stearic acid
$C_5H_{10}O_2$	Isovaleric acid	$C_{20}H_{40}O_2$	Arachidic acid
$C_6H_{12}O_2$	Caproic acid	$C_{22}H_{44}O_2$	Behenic acid
$C_8H_{16}O_2$	Caprylic acid	$C_{24}H_{48}O_2$	Lignoceric acid
$C_{10}H_{20}O_2$	Capric acid	$C_{24}H_{48}O_2$	Carnaübic acid
$C_{12}H_{24}O_2$	Lauric acid	$C_{24}H_{48}O_2$	Pisangcerylic acid
$C_{13}H_{26}O$	Ficocerylic acid	$C_{25}H_{50}O_2$	Hyænic acid (?)
$C_{14}H_{28}O_2$	Myristic acid	$C_{26}H_{52}O_2$	Cerotic acid
$C_{15}H_{30}O_2$	Isocetic acid (?)	$C_{30}H_{60}O_2$	Melissic acid
$C_{16}H_{32}O_2$	Palmitic acid	$C_{33}H_{66}O_2$	Psyllostearylic acid

II. Acids of the series $C_nH_{2n-2}O_2$. Acids of the Acrylic or Oleic Series.

$C_5H_8O_2$	Tiglic acid	$C_{18}H_{34}O_2$	Isooleic acid
$C_{12}H_{22}O_2$	not named	$C_{18}H_{34}O_2$	Rapic acid
$C_{14}H_{26}O_2$	not named	$C_{19}H_{36}O_2$	Doeglic acid
$C_{16}H_{30}O_2$	Hypogæic acid	*$C_{19}H_{36}O_2$	Jecoleic acid
$C_{16}H_{30}O_2$	Physetoleic acid	$C_{22}H_{42}O_2$	Erucic acid
$C_{16}H_{30}O_2$	Lycopodic acid[1]	$C_{22}H_{42}O_2$	Brassidic acid
$C_{18}H_{34}O_2$	Oleic acid	$C_{22}H_{42}O_2$	Isoerucic acid
$C_{18}H_{34}O_2$	Elaïdic acid		

III. Acids of the series $C_nH_{2n-4}O_2$. Acids of the Linolic Series.

$C_{18}H_{32}O_2$	Linolic acid	$C_{18}H_{32}O_2$	Telfairic acid
$C_{18}H_{32}O_2$	Tariric acid	$C_{18}H_{32}O_2$	Elæomargaric acid
$C_{18}H_{32}O_2$	Millet oil acid		

[1] Aldepalmitic acid $C_{16}H_{30}O_2$ (Wanklyn, *Journ. Soc. Chem. Ind.* 1891, 212) has not been admitted to the above list on account of its doubtful existence.

* The existence of the acids marked with an * has been inferred from derivatives of such hypothetical acids.

IV. Acids of the series $C_nH_{2n-6}O_2$. Acids of the Linolenic Series.

$C_{18}H_{30}O_2$ Linolenic acid	*$C_{18}H_{30}O_2$ Jecoric acid
$C_{18}H_{30}O_2$ Isolinolenic acid	

V. Acids of the series $C_nH_{2n-8}O_2$.

$C_{14}H_{20}O_2$ Isanic acid	*$C_{17}H_{26}O_2$ Therapic acid

VI. Acids of the series $C_nH_{2n}O_3$. Hydroxylated Acids.

$C_{16}H_{32}O_3$ Lanopalmic acid	$C_{31}H_{62}O_3$ Cocceric acid
$C_{21}H_{42}O_3$ not named	

VII. Acids of the series $C_nH_{2n-2}O_3$. Acids of the Ricinoleic Series.

$C_{18}H_{34}O_3$ Ricinoleic acid	$C_{18}H_{34}O_3$ Ricinic acid
$C_{18}H_{34}O_3$ Isoricinoleic acid	$C_{18}H_{34}O_3$ Acid in Quince oil
$C_{18}H_{34}O_3$ Ricinelaïdic acid	

VIII. Acids of the series $C_nH_{2n}O_4$. Dihydroxylated Acids.

$C_{18}H_{36}O_4$ Dihydroxystearic acid	$C_{30}H_{60}O_4$ Lanoceric acid

IX. Acids of the series $C_nH_{2n-2}O_4$.

$C_{22}H_{42}O_2$ Japanic acid

B. Alcohols

I. Alcohols of the series $C_nH_{2n+2}O$. Alcohols of the Ethane Series.

$C_{13}H_{28}O$ Pisangceryl alcohol	$C_{26}H_{54}O$ Ceryl alcohol
$C_{16}H_{34}O$ Cetyl alcohol (Ethal)	$C_{27}H_{56}O$ Isoceryl alcohol (?)
$C_{18}H_{38}O$ Octodecyl alcohol	$C_{30}H_{62}O$ Myricyl (Melissyl) alcohol
$C_{24}H_{50}O$ Carnaübyl alcohol	$C_{33}H_{68}O$ Psyllostearyl alcohol
$C_{24}H_{50}O$ or $C_{25}H_{52}O$ not named	

II. Alcohols of the series $C_nH_{2n}O$. Alcohols of the Allylic Series.

$C_{12}H_{24}O$ Lanolin alcohol	$C_{15}H_{30}O$ not named

III. Alcohols of the series $C_nH_{2n-6}O$.

$C_{17}H_{28}O$ Ficoceryl alcohol

IV. Alcohols of the series $C_nH_{2n+2}O_2$. Alcohols of the Glycolic Series.

$C_{25}H_{52}O_2$ not named	$C_{30}H_{62}O_2$ Cocceryl alcohol

* The existence of the acids marked with an * has been inferred from derivatives of such hypothetical acids.

V. Alcohols of the series $C_nH_{2n+2}O_3$.

$C_3H_8O_3$ Glycerol

VI. Alcohols of the Aromatic Series.

$C_{26}H_{44}O$ Cholesterol	$C_{26}H_{44}O$ Phytosterol
$C_{26}H_{44}O$ Isocholesterol	$C_{27}H_{44}O + H_2O$ Sitosterol

A. Acids

Occurrence of Fatty Acids

The fatty acids above enumerated are by no means equally distributed. Those fatty acids which contain an uneven number of carbon atoms (isovaleric, ficocerylic, isocetic, daturic, hyænic, tiglic acid, etc.) are of comparatively rare occurrence and mostly confined to some one individual fat. Indeed, some of those enumerated will not, perhaps, bear the light of modern investigation with its improved methods of research, and may have to share the fate of medullic,[1] moringic, theobromic,[2] crotonoleic,[3] umbellulic[4] acids, which must be considered as definitely removed from the list of fatty acids. The fatty acids of most fats contain exclusively an even number of carbon atoms. Amongst the latter, palmitic, stearic, and oleic acids predominate (linolic acid in the drying oils, and ricinoleic acid in castor oil) to such an extent that the chief part of most oils and fats consists of a mixture of the simple or mixed glycerides of these three acids. Glycerides of the lower fatty acids may occur conjointly with them, but in that case they are present in smaller quantities. Therefore a *large percentage* of a fatty acid other than palmitic, stearic, or oleic acid in a fat may always be looked upon as being characteristic of that fat, as will readily be seen from the following short summary :—

Acetic acid is stated to occur as a glyceride (triacetin) in small quantities in the seeds of the spindle-tree[5] (*Euonymus europæus*, L.). It has been found in small quantities in macassar oil.

Butyric acid occurs as a glyceride (butyrin) in cow butter to the extent of about 6 per cent; in smaller quantities it has been found in macassar oil.

Isovaleric acid is found as a glyceride in porpoise and dolphin oils.

Caproic acid occurs as caproin in butter fat and cocoa nut oil, together with caprylin and caprin. If butyrin, caproin, caprylin, and caprin conjointly exist to the extent of at least 1 to 2 per cent in a fat, that fat will be characterised by these glycerides. Thus, butter fat is specially remarkable for containing 8 per cent of these

[1] *Berichte*, 23. Ref. 493.
[2] *Ibid.* 16. 1103.
[3] *Journ. Soc. Chem. Ind.* 1895, 985.
[4] *Amer. Chem. Journ.* 1902, 327.
[5] *Jahresberichte*, 1851, 444.

glycerides, whilst the fats belonging to the cocoa nut oil class contain from 4 to 5 per cent.

The glyceride of *lauric* acid, laurin or laurostearin, is the chief constituent of the tangkallak fat from the Javanese tree *Cylicodaphne sebifera*, Bl.; it occurs also in laurel oil in large quantities, and in smaller amounts in cocoa nut oil.

Ficocerylic acid has been recently isolated from Pisang wax.

Myristic acid is found as a glyceride in nutmeg butter, liver fat, and as a constituent of a wax in wool wax; *isocetic* acid in the seeds of the purging nut (*Jatropha curcas*, L.); *daturic* acid in the oil of *Datura Stramonium*, and perhaps among the solid fatty acids of palm oil; *arachidic* acid in arachis (earth nut) oil; *behenic* acid in ben (behen) oil; and *lignoceric* acid in arachis oil.

Carnaübic acid occurs in carnaüba wax, and in wool wax; *pisangcerylic* acid in pisang wax; *cerotic* and *melissic* acids are found in the free state in beeswax, and the former also in Chinese wax as ceryl cerotate, and in wool wax. *Psyllostearylic* acid is a constituent of psylla wax.

Hyænic acid has been stated to occur in the glandular pouches of the striped hyæna as a glyceride.

Of the rarer acids belonging to the oleic series, *tiglic* acid occurs as a glyceride in croton oil, and, passing over the two unnamed acids $C_{12}H_{22}O_2$ and $C_{14}H_{26}O_2$ which have been found in the fat of cochineal, *hypogæic* acid in arachis oil, *physetoleic* acid and *doeglic* acid in sperm oil and in Arctic sperm (bottlenose) oil respectively as esters of higher alcohols; *erucic* and *rapic* acids occur as glycerides in rape oil.

Large quantities of the glyceride of *linolic* acid are characteristic of the so-called drying oils, and it is generally associated with the glycerides of *linolenic* and *isolinolenic* acids. *Tariric* acid occurs as a glyceride in the seeds of a Guatemalan shrub, *Picramnia*, and its isomeride *telfairic* acid amongst the fatty acids of Koëme oil. *Elæomargaric* acid has been found hitherto as a glyceride in the seeds of *Elæococca vernicia* only.

Of the acids of the series $C_nH_{2n-8}O_2$—*isanic* and *therapic*—but little is known as yet.

The hydroxylated acids *lanopalmic* acid, the acid $C_{21}H_{42}O_3$, and *cocceric* acid are constituents of wool wax, carnaüba wax, and of the wax of cochineal respectively. The glycerides of *ricinoleic* and *isoricinoleic* acids constitute the principal part of castor oil.

The first natural dihydroxylated acid, *dihydroxystearic* acid, has been detected in castor oil; another dihydroxylated acid, *lanoceric* acid, occurs in wool wax.

A naturally occurring dibasic acid—*japanic* acid—has been obtained from Japan tallow (Japan wax).

PROPERTIES OF FATTY ACIDS

Specific Gravities of Fatty Acids.—The specific gravities of the fatty acids at different temperatures will be found under the heading

of the individual acids. To indicate that the specific gravity decreases with the increase of the number of carbon atoms in the molecule, and that the specific gravities of the unsaturated acids are higher than those of saturated acids having the same number of carbon atoms, I give the following table :—

Acid.	Specific Gravity.
Acetic	1·0515 at 15 °C.
Butyric	0·9580 at 14 ,,
Isovaleric	0·9310 at 20 ,,
Caproic	0·9274 at 20 ,,
Caprylic	0·9100 at 20 ,,
Capric	0·8858 at 40 ,,
Lauric	0·875 at 43·6 ,,
Myristic	0·8622 at 53·8 ,,
Palmitic	0·8527 at 62 ,,
Stearic	0·8454 at 69·2 ,,
Cerotic	0·8359 at 79 ,,
Oleic	0·8540 at 78·4 ,,
Elaïdic	0·8505 at 79·4 ,,
Erucic	0·8602 at 55·4 ,,

Solidifying and Melting Points of Fatty Acids.—The lower members of the acetic acid series, including caprylic acid, and further oleic, rapic, doeglic, linolic, and ricinoleic acids are liquid at the ordinary temperature; all the others are solid. The following table contains the solidifying and melting points of the more important acids :—

[TABLE

Acid.	Solidifying Point. °C.	Melting Point. °C.
Acetic	+17·5	...
Butyric	−19	−6·5
Isovaleric	−57	−51
Caproic	−8	...
Caprylic	12	16·5
Capric	...	31·3
Lauric	...	43·6
Ficocerylic	...	...
Myristic	...	53·8
Isocetic	...	55
Palmitic	62·6	62·62
Daturic	...	54·5
Stearic	69·3	69·32
Arachidic	79-77	77·0
Behenic	...	83-84
Lignoceric	...	80·5
Carnaübic	69-67	72·5
Pisangcerylic	...	72
Hyænic	...	77-78
Cerotic	...	77·8
Melissic	...	91
Psyllostearylic	...	94-95
Tiglic	...	64·5
Hypogæic	...	33·0
Gaïdic	...	39
Physetoleic	...	30·0
Oleic	...	14
Isooleic	...	44-45
Elaïdic	...	44·5
Erucic	...	33-34
Isoerucic	...	54-56
Brassidic	...	65-66
Elæomargaric	...	43·4
Elæostearic	...	71
Tariric	...	50·5
Linolic	below −18	...
Isanic	...	41
Lanopalmic	...	87-88
Cocceric	...	92-93
Ricinoleic	6-10	4-5
Ricinelaïdic	...	52-53
Ricinic	...	81
Dihydroxystearic	...	141-143
Lanoceric	103-101	104-105
Japanic	...	117·7

The solidifying points of mixed fatty acids are of great importance in the examination of fats; they are more characteristic than the melting points of such mixed fatty acids. It is not possible to infer the *solidifying point of a mixture of pure fatty acids* from the solidifying points of the individual fatty acids, as is clearly brought out by the numbers given in the following table. Mixtures of pure fatty acids are apt to form "eutectic" compounds, behaving, as regards melting and solidifying points, like pure chemical substances. Thus, a mixture of 47·5 per cent of stearic and 52·5 per cent of palmitic acids cannot be resolved by crystallising from alcohol into its com-

ponents. Nor can the melting point of a mixture of two fatty acids be calculated from the melting points of the constituents. As a rule, the melting point lies considerably below the calculated one, sometimes even below the melting point of the lowest melting acid. The following tables will illustrate this fact:—

Solidifying Points of Mixtures of Palmitic Acid with Stearic Acid (de Visser)

Palmitic Acid. Per cent.	Stearic Acid. Per cent.	Solidifying Point. °C.	Palmitic Acid. Per cent.	Stearic Acid. Per cent.	Solidifying Point. °C.
100	0	62·618	56	44	56·36
90	10	59·31	55	45	56·38
85	15	57·80	54	46	56·39
80	20	56·53	53	47	56·40
75	25	55·46	52	48	56·40
71	29	54·92	51	49	56·41
70	30	54·85	50	50	56·42
68	32	55·12	49	51	56·44
66	34	55·38	48	52	56·50
64	36	55·62	47	53	56·63
63	37	55·75	46	54	56·85
62	38	55·88	45	55	57·20
61	39	56·00	40	60	58·76
60	40	56·11	30	70	61·73
59	41	56·19	20	80	64·51
58	42	56·25	10	90	67·02
57	43	56·31	0	100	69·32

Melting Points of Mixtures of Lauric Acid with Myristic, Palmitic, and Stearic Acids (Heintz)

Lauric Acid. Per cent.	Myristic Acid.		Palmitic Acid.		Stearic Acid.	
	Per cent.	Melting Point.	Per cent.	Melting Point.	Per cent.	Melting Point.
		°C.		°C.		°C.
100	0	43·6	0	43·6	0	43·6
90	10	41·3	10	41·5	10	41·5
80	20	38·5	20	37·1	20	38·5
70	30	35·1	30	38·3	30	43·4
60	40	36·7	40	40·1	40	50·8
50	50	37·4	50	47·0	50	55·8
40	60	43·0	60	51·2	60	59·0
30	70	46·7	70	54·5	70	62·0
20	80	49·6	80	57·4	80	64·7
10	90	51·8	90	59·8	90	67·0
0	100	53·8	100	62·0	100	69·2

Melting Points of Mixtures of Myristic Acid with Palmitic and Stearic Acids (Heintz)

Myristic Acid. Per cent.	Palmitic Acid.		Stearic Acid.	
	Per cent.	Melting Point.	Per cent.	Melting Point.
		°C.		°C.
100	0	53·8	0	53·8
90	10	51·8	10	51·7
80	20	49·5	20	47·8
70	30	46·2	30	48·2
60	40	47·0	40	50·4
50	50	47·8	50	54·5
40	60	51·5	60	59·8
30	70	54·9	70	62·8
20	80	58·0	80	65·0
10	90	60·1	90	67·1
0	100	62·0	100	69·2

Melting Points of Mixtures of Palmitic Acid with Stearic Acid

Palmitic Acid. Per cent.	Stearic Acid. Per cent.	Melting Point.	
		Heintz.	Hehner and Mitchell.
		°C.	°C.
100	0	62·0	61·8
90	10	60·1	59·0
80	20	57·5	56·5
70	30	55·1	54·2
67·5	32·5	55·2	54·5
60	40	56·3	55·5
50	50	56·6	55·6
40	60	60·3	59·4
30	70	62·9	61·5
20	80	65·3	64·2
10	90	67·2	66·5
0	100	69·2	68·5 [1]

Melting Points of Mixtures of Palmitic and Cerotic Acids (Lewkowitsch)

Palmitic Acid. Per cent.	Cerotic Acid. Per cent.	Melting Point °C.
100	0	60·0
90	10	56·0
85	15	56·5
75	25	60·5
60	40	65·5
50	50	68·6
40	60	70·0
0	100	78·5

[1] This melting point is decidedly too low for pure stearic acid.

Boiling Points of Fatty Acids.—Of the more frequently occurring fatty acids, only the following can be distilled under ordinary pressure without decomposition :—

Acid.	Boiling Point. °C.
Butyric	162·3
Caproic	202-203
Caprylic	236-237
Capric	268-270

These acids are readily volatilised with water vapours from their aqueous solutions, hence they are also termed *volatile* fatty acids, in contradistinction to the *non-volatile* acids. Lauric acid occupies an intermediate position between the two classes. All the others, when distilled at ordinary pressure, undergo partial decomposition, and amongst the products of destructive distillation, hydrocarbons of the ethane series are found, a fact which forms the main chemical argument in favour of *Höfer-Engler's* theory of the formation of petroleum from the oils of marine animals. Under diminished pressure, however, and with the aid of superheated steam, many fatty acids may be distilled without suffering decomposition. In practice, the latter method is largely used for the preparation of the distilled fatty acids. More recently the two methods have been combined.

At a pressure of 100 mm. and 15 mm., and *in vacuo*, the following boiling points have been found :—

Acid.	Boiling Point at 100 mm. Pressure. °C.	Boiling Point at 15 mm.[1] Pressure. °C.	Boiling Point *in vacuo*.[1] °C.
Lauric . . .	225	176	102
Myristic . .	250·5	196·5	121-122
Palmitic . .	271·5	215	138-139
Daturic . .	...	223-225	...
Stearic . . .	291	232·5	154·5-155·5
Hypogæic[2] .	...	236	...
Oleic . . .	285·5-286	232·5	153
Elaïdic . . .	287·8-288	234	154
Erucic . . .	...	264	179
Brassidic . .	...	265	160
Ricinoleic . .	...	250	...
Ricinic . . .	...	250-252	...

Solubility of Fatty Acids.—The lowest members of the acetic series are miscible with water in every proportion; caproic acid is soluble in water, but not miscible with it. The solubility in water decreases rapidly with the increase of the number of carbon atoms in the molecule. Caprylic acid requires for its solution 400 parts of boiling water; on cooling, the acid separates out almost completely. Capric and lauric acids are very slightly soluble in boiling water;

[1] Krafft and Weilandt, *Berichte*, 1896 (29), 1324.
[2] Bodenstein, *Ibid.* 1894, 3399

the higher acids are altogether insoluble in water. Taking the solubility as a basis for classification, we may subdivide the fatty acids, for analytical purposes, into *soluble* and *insoluble* fatty acids. The acids up to capric acid are termed *soluble* fatty acids; the higher fatty acids from myristic acid upwards are the *insoluble* fatty acids. Lauric acid occupies, also as regards solubility, an intermediate position.

All fatty acids, without exception, are soluble in hot alcohol; they are also readily soluble in ether and petroleum ether.

Refractive Index of Fatty Acids.—The magnitude of the refractive indices increases with the increase of the number of carbon atoms in the molecule. The unsaturated fatty acids show a higher refraction than the saturated acids of the same number of carbon atoms. This is shown by the following short table; further details will be found under the heading of each individual acid.

Acid.	Refractive Index at °C.
Butyric	1·39906 at 20
Caproic	1·41635 at 20
Caprylic	1·42825 at 20
Capric	1·42855 at 40
Lauric	1·42665 at 60
Myristic	1·43075 at 60
Palmitic	1·42693 at 80
Stearic	1·43003 at 80
Oleic	1·44710 at 60

Viscosity of Fatty Acids.—Since viscosimetric methods have been proposed for the examination of oils and fats, it may be found useful to record here the following viscosimetric constants. From the values given in the table, it is evident that the viscosity increases with the molecular weight.

Viscosimetric Constants of Fatty Acids (Pribram and Handl)

Fatty Acid.	Molecular Weight.	Specific Viscosity at		
		10° C.	30° C.	50° C.
Propionic	74	70·3	51·5	49·9
Butyric	88	110·2	77·4	57·6
Valerianic	102	152·4	103·3	71·5
Caproic	116	222·2	139·7	97·8

With regard to the following physical characters: specific heat, heat of neutralisation, latent heat, surface tension, *Guillot's*[1] pamphlet should be consulted. As to heat of combustion, cp. p. 223.

Salts of Fatty Acids.—The fatty acids readily combine with solutions of caustic soda and caustic potash to form "soaps." In

[1] *Propriétés Physiques de la Série Grasse.* Paris. Baillière et fils, 1895.

dilute aqueous solution the chemical union does not take place in molecular proportions, so that free fatty acids and free alkali can co-exist to a certain extent (*see* below, "Hydrolysis of Soaps"). In alcoholic solutions, however, the combination takes place in stoichiometric proportions. The carbonates of the alkali metals react with fatty acids in aqueous solution at somewhat elevated temperatures, forming salts of fatty acids with evolution of carbonic acid.

Since in commercial analysis the fatty acids are frequently estimated by titration with solutions of alkali, it is important to consider in some detail the behaviour of the fatty acids towards the indicators used in volumetric analysis. From the large number of indicators which have been proposed from time to time, I select for the analysis of fats, methylorange and phenolphthalein, which will be found quite sufficient for all purposes. Tincture of litmus (the place of which has lately been taken by lacmoïd) still enjoys some popularity, and may be used in conjunction with the above-named two indicators.

Methylorange[1] dissolves in water to a yellow liquor, which turns crimson on the addition of a strong acid, appearing yellowish-red in deep layers, a salt being formed with the acid. Thus with hydrochloric acid the salt $C_6H_4{<}\begin{smallmatrix}-SO_3H\\-H=N-C_6H_4N(CH_3)_2\,.\,HCl\end{smallmatrix}$ is obtained. The change from the yellowish colour of the neutral solution to the red is especially sharp in very dilute solutions. Weak acids, such as carbonic acid, do not change the colour; therefore, it is possible to titrate carbonates, using methylorange as an indicator, without it being required to drive off the liberated carbonic anhydride by boiling. The acid carbonates of the alkalis are alkaline to methylorange (difference from phenolphthalein). This indicator is specially suitable for the estimation of mineral acids, and offers the further advantage that it can, and indeed must, be used in the cold. Boric acid, however, is not affected by methylorange; even concentrated aqueous solutions of the acid are not reddened.

The soluble fatty acids also redden a solution of methylorange, but on titrating with normal alkali, the end-reaction is not sharp, and the red colour disappears when considerable quantities of free fatty acids are still in the solution; therefore methylorange cannot be used for titrating soluble fatty acids, not even acetic acid.[2] The insoluble fatty acids, as stearic or oleic, do not affect this indicator at all in

[1] Prepared from diazobenzene sulphonic acid $C_6H_4{<}\begin{smallmatrix}-N=N\\-SO_3\end{smallmatrix}{>}$ and dimethylaniline. It is the ammonium salt of dimethylaniline-azobenzenesulphonic acid, the constitution of which is expressed by the formula—

$$C_6H_4{<}\begin{smallmatrix}-SO_3NH_4\\-N=N-C_6H_4N(CH_3)_2.\end{smallmatrix}$$

According to *Lunge*, tropæolin 00 or 000 is often sold as methylorange. I have occasionally met with methylorange having such strong alkaline reaction, that four drops of a $\frac{1}{10}$ per cent solution required 0·1 c.c. of normal acid for neutralisation. Methylorange should, therefore, always be examined before use.

[2] *Schidrowitz* (*Analyst*, 1903, 234) showed that acetic acid can be titrated with methylorange as an indicator, if alcohol be added to the solution.

their alcoholic solution, nor do they act on it when shaken in the liquid state with an aqueous solution of methylorange.

It is, therefore, possible to titrate mineral acids in presence of the higher fatty acids, using methylorange as an indicator. Methylorange offers the further advantage, that it can be employed along with another indicator. Thus, in a mixture of mineral and higher fatty acids, the mineral acid may be estimated first by using methylorange as an indicator; then after adding phenolphthalein, the higher fatty acids may be titrated.

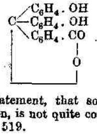
The solution of the indicator is prepared by dissolving 1 grm. in 1000 c.c. of water. Four drops of this solution are sufficient for every 100 c.c. of the liquid to be titrated.

Phenolphthalein.[1]—This indicator can be obtained of sufficient purity in commerce. To prepare the solution required for volumetric analysis, *1 grm. is dissolved in 100 c.c. of 95 per cent alcohol.* Two drops of this indicator will be found sufficient for every 100 c.c. of the solution. The alcoholic solution of phenolphthalein is yellowish, and turns pink on the addition of the slightest quantity of a fixed alkali, owing to the formation of a salt. This salt is decomposed completely even by weak acids, therefore the insoluble fatty acids may be titrated in their alcoholic solutions in presence of this indicator. Ammonia does not give a sensitive colour reaction with phenolphthalein, and hence is unsuitable for the titration of fatty acids. Phenolphthalein may also be used for the titration of the soluble fatty acids in the same way as litmus, which is, however, preferred by some chemists. Due regard should be paid to the sensitiveness of phenolphthalein to carbon dioxide, and to the fact that the acid carbonates of the alkalis do not act on phenolphthalein like the carbonates;[2] it is therefore absolutely necessary to remove the carbonic dioxide by boiling. When standardising acids and alkalis with the aid of phenolphthalein, this possible source of error should especially be guarded against.

Litmus.—Tincture of litmus may be used in the analysis of fats for titrating the volatile fatty acids, mineral acids, caustic alkalis, carbonates, etc. The statement made by *Rechenberg*,[3] that the salts

[1] This is prepared by heating to 115°-120° C., for ten to twelve hours, a solution of 250 grms. of phthalic anhydride $C_6H_4{<}^{-CO}_{-CO}{>}O$ in 200 grms. of concentrated sulphuric acid, with 500 grms. of phenol $C_6H_5 . OH$. The hot melt is poured into boiling water, and washed with boiling water until the odour of phenol has disappeared. The residue is of sufficient purity to be at once used as an indicator.

The chemical constitution of phenolphthalein is expressed by the formula—



[2] The frequently repeated statement, that sodium bicarbonate does not redden phenolphthalein in aqueous solution, is not quite correct.

[3] *Journ. prakt. Chemie*, 1884, 519.

formed by the union of volatile fatty acids with alkalis and alkaline earths—especially those of butyric acid—show in their aqueous solution strongly alkaline reaction, has not been confirmed by the author's experience. It is quite possible to titrate butyric acid, using litmus as an indicator. The change is somewhat gradual, but perfectly distinct.

In common parlance, we generally understand under the term "soaps" the alkali salts of the non-volatile fatty acids, whereas the term "metallic salts" denotes the salts of the heavy metals. I shall consider the salts of the fatty acids under the following two large groups:—(1) Salts of the Alkali-Metals, including the Ammonia Soaps; (2) Salts of the Alkaline Earths, and of the heavy metals.

(1) *Salts of the Alkali-Metals*

The normal salts of the saturated acids have the general formula $C_nH_{2n+1}CO.OM$, where M stands for Na or K. In alcoholic solution these salts are neutral to phenolphthalein. Besides the neutral salts there exist also acid salts of the formula $C_nH_{2n+1}CO.OM, C_nH_{2n}O_2$; dissolved in hot alcohol these show acid reaction to phenolphthalein.

The alkali-salts of the fatty acids are remarkable in their behaviour to water.

The salts of the lowest members of the series are easily soluble in water. Thus the alkali salts of butyric acid are deliquescent, and those of capric acid are still very easily soluble in water at the ordinary temperature. But the solubility in water decreases as the molecular weight of the fatty acids increases; thus the alkali salts of palmitic and stearic acid are no longer soluble in cold water. They dissolve, however, when boiled with not too large a quantity of water, to a clear solution, which solidifies, on cooling, to a mucilaginous mass, representing the normal salts of the fatty acids, or at any rate approximately so.

On diluting the clear hot solutions with water they become turbid, and, on shaking, a lather is produced which persists for some time. The turbidity is due to the dissociation of normal salt into caustic alkali and free fatty acid. This dissociation, termed *hydrolysis of soap*, is a very gradual one, depending on the amount of water present and also on the temperature.

The free alkali remains in solution, and the free fatty acid combining with non-hydrolysed salt separates, forming an acid salt, *i.e.* a salt containing more than one equivalent of acid for one equivalent of alkali, presumably in association with some undissociated salt.

Chevreul, who first studied this property of alkali-metal soaps, found that a solution of one part of neutral potassium stearate, $C_{18}H_{35}O_2.K$, in 20 parts of boiling water, treated with an additional 1000 parts of boiling water yields, on cooling, an acid salt of the composition $C_{18}H_{35}O_2K.C_{18}H_{36}O_2$—*potassium bistearate*—whilst free alkali and an infinitesimal quantity of stearic acid remain in solution. Similarly, neutral sodium stearate dissolved in 2000 to 3000 parts of

boiling water yields, on cooling, an acid salt of the composition $C_{18}H_{35}O_2Na \cdot C_{18}H_{36}O_2$—*sodium bistearate.* Neutral oleate, however, requires a very large quantity of water and a low temperature to become dissociated; the difference between oleic acid on the one hand, and palmitic and stearic on the other hand, is so marked that an approximate method of separation may be based on this property.

The potassium bistearate can be further dissociated by treatment with water into a more acid salt, presumably of the composition of a quadro-stearate.

The amount of alkali thus set free under given conditions can be determined quantitatively by salting out the "curd," filtering off and washing with brine, dissolving the curd in absolute alcohol, and determining the acidity by titration with alkali, using phenolphthalein as an indicator.

Alder Wright and *Thompson*[1] derived from a series of observations the results contained in the following table. I have arranged the fatty acids in the order of their molecular weights:—

Fatty Acids.	Mean Molecular Weight.	Hydrolysis brought about by x Molecules of Water.				
		$x=150$	$x=250$	$x=500$	$x=1000$	$x=2000$
Crude lauric	195	3·75	4·5	5·4	6·45	7·1
(Cotton seed oil acids	250[2]	2·25	3·0	5·0	7·5	9·5)
Nearly pure palmitic	256	1·45	1·9	2·6	3·15	3·75
(Palm-oil-tallow acids	271	1·1	1·55	2·6	4·1	5·3)
Pure oleic	282	1·85	2·6[2]	3·8	5·2	6·65
Pure stearic	284	0·7	1·0	1·7	2·6	3·55

The numbers represent the quantities of Na_2O set free by hydrolysis, calculated *for 100 parts of Na_2O contained in the soap in* combination with fatty acid, x molecules of water being used for one of anhydrous soap.

If we look at the numbers given for lauric, palmitic, and stearic acids only, it would appear that the sodium salts of the fatty acids are decomposed with greater ease, the *lower* their molecular weight. But on the one hand the behaviour of oleic acid does not conform with this rule, and on the other hand *Thomsen*[3] has shown that sodium acetate is not measurably dissociated by water. (Cp., however, p. 81.)

Rotondi[4] explained the action of water on soap in the following manner: The neutral (commercial) soaps, on being dissolved, are decomposed into basic and acid salts; the latter are insoluble in cold, and only slightly soluble in hot water. The acid salts are not dialysable, and can, therefore, be separated from the former which readily pass through membranes. The basic soaps are completely soluble in cold and hot water, and are entirely precipitated by sodium

[1] *Journ. Soc. Chem. Ind.* 1885, 630.
[2] This appears to be somewhat low.
[3] *Thermochemische Untersuchungen*, i. 372.
[4] *Journ. Soc. Chem. Ind.* 1885, 601.

chloride without loss of alkali; their solutions dissolve acid soaps on heating, but become turbid on cooling.

Rotondi's views have been shown by *Krafft* and *Stern*[1] to be erroneous. They repeated *Chevreul's* experiment with pure sodium palmitate (2 grms.), and obtained the following result:—

1 Part of Sodium Palmitate containing 8·27 per cent Na	
Boiled with parts Water	Yielded, on cooling, salt containing Na.
	Per cent.
200	7·01
300	6·84
400	6·60
450	6·32
500	6·04
900	4·20

In order to obtain an insight into the approximate composition of the separated salts, the following table may be consulted:—

Salts of the formula	Containing Na. Per cent.
$C_{16}H_{31}O_2Na$	8·27
$3C_{16}H_{31}O_2Na + C_{16}H_{32}O_2$	6·33
$C_{16}H_{31}O_2Na + C_{16}H_{32}O_2$	4·31
$C_{16}H_{31}O_2Na + 3C_{16}H_{32}O_2$	2·20

Similar experiments with pure sodium stearate gave the following result:—

1 Part of Sodium Stearate containing 7·52 per cent Na		
Boiled with parts Water	Yielded, on cooling, salt containing Na.	
	Per cent.	
	I.	II.
200	6·34	6·27
300	5·81	5·71

Sodium bistearate $C_{18}H_{35}O_2Na + C_{18}H_{36}O_2$ contains 3·89 per cent Na.

From these experiments the conclusion must be drawn that *hydrolysis increases with the molecular weight of the fatty acids;* this is in direct opposition to the conclusions derived from *Alder Wright* and *Thompson's* more complete series of observations detailed above (p. 76).

As shown already, oleic acid occupies an exceptional position as regards hydrolysis of its salts. This has been confirmed by *Krafft* and *Stern*, according to whose observation pure neutral sodium oleate dissolves to a *clear* solution in about 10 parts of *cold* water, which does not yield a sensibly turbid solution even on dilution with 900

[1] *Berichte*, 1894, 1747.

parts of water, whereas the sodium bioleate, $C_{18}H_{33}O_2Na + C_{18}H_{34}O_2$, is immediately dissociated by cold water. In order to hydrolyse oleates, much larger quantities of water are required; at the same time the temperature must be lowered considerably.

The solid elaïdic acid, however, simulates stearic acid in its behaviour, as the following observations prove:—

1 Part of Sodium Elaïdate containing 7·56 per cent Na	
Boiled with parts Water	Yielded, on cooling, salt containing Na.
	Per cent.
300	5·80
1500	3·24

In the light of these experiments, the commercial soaps, consisting practically of palmitates, stearates, and oleates, would yield, on treatment with large quantities of water, acid palmitates and stearates as precipitates, whereas free alkali and oleates would remain in solution. The solution would thus contain soap *plus* free alkali, a fact which has been taken by *Rotondi* as a proof for the existence of basic soaps in solution. Besides, direct experiments made with a view to preparing synthetically basic salts from oleic acid failed completely, and on hydrolysing pure sodium palmitate with 900 parts of water, not a trace of palmitic acid could be detected in the cold supernatant solution.

The direct proof that free fatty acid and free alkali co-exist in a dilute solution in the hot was given by extracting a solution of not completely hydrolysed normal sodium palmitate with toluene, when free palmitic acid was obtained.

The hydrolysis of soaps becomes complete according to *Krafft* and *Wiglow*,[1] if the one of the two components of the normal salt—say fatty acid—is removed, as by shaking out repeatedly with toluene.

This statement, however, is not consistent with the fact explained below, namely, that free alkali prevents hydrolysis. Theoretically, it must, therefore, be expected that in a soap solution an equilibrium would be established between the hydrolysing tendency of water and the opposite tendency of alkali to prevent hydrolysis. Hence it would follow that if a certain amount of water be added to a soap solution, a definite quantity only, but not the whole quantity of fatty acids, can be extracted, the remainder of the fatty acids being retained in the solution as soap, this soap being protected from further hydrolysis by the amount of alkali set free in consequence of the hydrolysis that had taken place so far. In order to test this view by experiment,[2] I prepared anhydrous soaps from pure palmitic acid, pure stearic acid, and commercial oleic acid (containing about 8 per cent of solid acids). Two series of experiments were made with *one gram of each* anhydrous soap; in the one series the soaps were

[1] *Journ. Soc. Chem. Ind.* 1896, 206. [2] Unpublished experiments.

dissolved in 400 cc. of water, and in the second series in 900 cc. of water. The soap solutions were boiled under a reflux condenser, and then shaken out with toluene. The boiling and shaking out was repeated eight times; the toluene was then evaporated and the free fatty acids recovered from it and weighed. The alkali in the soap solutions was determined by titration in three stages; the solutions were first titrated, using phenolphthalein as an indicator in the cold. They were then boiled, and titrated after boiling, again using phenolphthalein as an indicator. Finally the solutions were titrated with methylorange as an indicator. The amounts of alkali so found are set out in the following table. The fatty acids recovered from the toluene solutions were weighed and calculated to anhydrides; the numbers are given in the following table. For comparison I have added the theoretical amounts of alkali and anhydrides.

Hydrolysis, by means of Water, of 1 grm. of pure Anhydrous Soap (Lewkowitsch)

Na_2O.	From					
	Oleic Acid (commercial).		Stearic Acid.		Palmitic Acid.	
	400 cc. water. Per cent.	900 cc. water. Per cent.	400 cc. water. Per cent.	900 cc. water. Per cent.	400 cc. water. Per cent.	900 cc. water. Per cent.
By phenolphthalein, in the cold .	3·93	2·87	7·83	4·32	5·96	4·13
,, ,, after boiling .	3·25	5·9	0·23	3·76	5·19	7·03
By methylorange	3·18	1·38	2·2	2·93	0·60	0·61
Total Na_2O found . . .	10·36	10·15	10·26	11·01	11·75	11·77
Theory	10·197		10·03		11·15	
Fatty Anhydrides—						
Hydrolysed	77·369	75·59	85·47	85·014	81·29	82·97
Not hydrolysed	9·37	5·25	2·71	3·3	1·94	1·96
Insoluble in water and ether .	0·17	0·84	1·43	0·18	1·5	0·29
Total found	86·709	81·68	89·61	88·494	84·73	85·22
Theory	89·803		89·87		88·85	

It will be seen from the above experiments that the quantity of soda found is slightly greater than theory requires; this can easily be explained by the action of the water on the glass vessels. The amount of fatty anhydrides found is, in the case of oleic acid, much below theory, which must be due to oxidation that had taken place on drying the oleic acid. Although also in the other two cases the agreement between experiment and theory is not as good as might be expected (owing to the large quantity of solvent used, and the number of operations through which the small quantity of fatty acids had to be put), still the experiments bear out fully the theoretical

postulate that complete hydrolysis is not possible. In the case of palmitic acid the hydrolysis had reached a remarkably high degree, so that the statements of *Krafft* and *Wiglow*, who worked especially with palmitic acid, can be readily explained.

It is apparent from the foregoing notes that oleic acid behaves differently from the solid fatty acids and even from elaïdic acid, *with which it is isomeric. This difference, however, disappears if not* only the one factor, which has been considered hitherto exclusively, viz. the proportion of water, is taken into account, but if proper regard is had to the temperature. For *Krafft* and *Wiglow*[1] observed that the temperature at which the separation of acid salts commences always lies below the melting point of the corresponding fatty acid. I have compiled the following table from the earlier experiments of *Krafft and Wiglow, in which a 1 per cent solution of the sodium* salt was examined, and some later experiments by *Krafft*.[2] I have also corrected the melting points of the free acids where required.

Sodium Salt of	I. Temperatures of Separation from Solutions, containing per cent.				II. Temperature of Separation from 1 per cent Solution.	III. Melting Point of Acid.	IV. Difference, III.-II.	V. Melting Points of the Dry Salts.
	25	20	15	10				
	°C.	°C.	°C.	°C.	°C.	°C.		°C.
Stearic acid	...	*69*	*68*	*68-67*	*60*	*69·4*	*9·2*	*about 260*
Palmitic ,,	...	62-61·8	...	...	45	62·0	17·0	,, 270
Myristic ,,	...	53-52	...	...	31·5	53·8	22·3	,, 250
Lauric ,,	45-42	about 36	...	...	11	43·6	32·6	255-260
Elaïdic	...	45·5-44·8	...	...	35	44·0	9·0	225-227
Oleic	13-6	...	...	...	0	14·0	14·0	232-235
Erucic	...	35-34	...	...	27	33·5	6·5	230-235
Brassidic	...	56	...	...	42	65·5	23·5	245-248

From these numbers the following rule has been derived: The temperatures of crystallisation of soaps always lies below the melting point of their free fatty acid, and the difference between both temperatures increases as they descend in the homologous series.

It will thus be seen that oleic acid falls in line with the other acids, and that, *e.g.*, a hot solution of sodium palmitate behaves like a cold solution of sodium oleate.

From a series of observations undertaken by *Krafft* and *Wiglow*[3] with a view to determining the molecular weight of soaps by the ebullioscopic method, it appears that the sodium salts of the lower fatty acids raise the boiling point of water by twice the normal value; this is explained by assuming that each molecule is hydrolysed into free fatty acid and sodium hydroxide, as indicated by the following equation :—

$$\underset{\text{Sodium Acetate.}}{C_2H_3O_2Na} + H_2O = C_2H_4O_2 + NaOH.$$

[1] *Journ. Soc. Chem. Ind.* 1896, 206. [2] *Berichte*, 1899, 1598.
[3] *Ibid.* 1896, 1329.

The sodium salts of the higher fatty acids do not raise the boiling point of water at *all*; the solutions solidify on cooling to gelatinous masses, and thus show the characteristic behaviour of colloïds.

The observations referred to are reproduced in the following table :—

Sodium Salts of Acid.	Formula.	Parts of Salt in 100 parts of Water.	Molecular Weight. Apparent.	Molecular Weight. Normal.	Apparent Mol. W. / Normal Mol. W.
Acetic	$C_2H_3O_2Na$	0·9 25·2	50·5 40·3	82	0·6 0·5
Propionic	$C_3H_5O_2Na$	3·8 19·8	51·7 46·2	96	0·6 0·5
Caproic	$C_6H_{11}O_2Na$	3·5 20·6	72·8 77·9	138	0·52 0·56
Nonylic	$C_9H_{17}O_2Na$	3·4 20·4	144·1 285·5	180	0·8 1·58
Lauric	$C_{12}H_{23}O_2Na$	3·3 16·1	474 507	222	2·13 2·28
Palmitic	$C_{16}H_{31}O_2Na$	16·4 25·0	about 1060 approaching ∞	278	about 4 approaching ∞
Stearic	$C_{18}H_{35}O_2Na$	abt. 16·0 27	about 1500 approaching ∞	306	about 5 approaching ∞
Oleic	$C_{18}H_{33}O_2Na$	26·5	approaching ∞	304	approaching ∞

The numbers given in the last column are, in the opinion of *Krafft* and *Wiglow*, a measure of the dissociation brought about, and thus show in a general way that the salts of the lowest fatty acids are hydrolysed in the hot, those of the higher acids already in the cold, whereas laurates occupy an intermediate position.

In the case of acetic acid at least, it is certainly very difficult to agree with the views of these chemists, since acetic acid can be determined quantitatively by titration with alkali in aqueous solutions. In the case of the higher fatty acids which can no longer be titrated in aqueous solutions, their opinions become more acceptable, especially so in view of the experiments described above.

The hydrolysis of sodium stearate might then be described in the following manner :—

$$C_{18}H_{35}O_2 . Na + H_2O \rightleftarrows C_{18}H_{35}O_2 . H + NaOH$$

expressing the fact that an equilibrium is established between free stearic acid, free caustic soda, and sodium stearate.

As regards the values given for the first three acids in the last column, showing that the molecular weights are apparently only half of the theoretical ones, the modern ionisation theory seems to afford the better explanation, namely, that the salts are broken up into two ions, the sodium ion and the fatty acid ion.[1]

The hydrolytic action of water is retarded by the addition of **free alkali**. The following table due to *Alder Wright* and *Thompson*, which

[1] Cp. Kahlenberg and Schreiner, *Zeit. physik. Chemie*, 1898 (27), 552.

should be compared with the one given above, p. 76, clearly illustrates this well-known fact (*practice of soap-making*).

Fatty Acids.	Extra Na_2O added to solution per 100 as combined soap.	Hydrolysis brought about by x Molecules of Water.		
		$x=150$	$x=250$	$x=2000$
Crude lauric	11·0	1·1	1·6	2·0
Cotton seed oil acids . .	15·0	nil	nil	6·5
Stearic and oleic (from tallow)	20·0	nil	nil	nil

Alcohol also exercises a retarding influence on the hydrolysis. Absolute alcohol, as also alcohol of 95 to 90 per cent, dissolve neutral soaps without causing dissociation. This is proved by the following table, which I have collated from the determinations of the molecular weights of normal soaps in solutions of anhydrous alcohol by *Krafft*.[1]

Salt.	Formula.	Calculated Molecular Weight.	Theoretical Molecular Weight.
Potassium formate . .	CHO_2K	87·60	84·16
,, acetate . .	$C_2H_3O_2K$	93·3-96·7	98·18
,, heptylate . .	$C_7H_{13}O_2K$	153·7-156·5	168·28
Sodium laurate . . .	$C_{12}H_{23}O_2Na$	237·2	222·3
,, myristate . . .	$C_{14}H_{27}O_2Na$	253	250·3
,, palmitate . . .	$C_{16}H_{31}O_2Na$	282·6	278·4
,, oleate . . .	$C_{18}H_{33}O_2Na$	301·3-345·9	304·4
Potassium oleate . . .	$C_{18}H_{33}O_2K$	347	320

If, however, water be added to an alcoholic soap solution, hydrolysis is brought about, in accordance with the quantity of water added. (This is easily demonstrated by adding a drop of phenolphthalein solution.) *Kanitz*[2] has shown that in order to prevent hydrolysis, the alcoholic soap solution must contain at least 40 per cent of 100 per cent alcohol. From concentrated alcoholic solutions the soaps separate on cooling, as a rule, in a jelly-like mass, which, however, becomes crystalline on standing for some time.

Amyl alcohol is able to prevent hydrolysis, if present in an aqueous solution to the extent of 15 per cent.

Glycerol also causes a diminution of the amount of hydrolysis brought about by water.

The presence of **salts** diminishes the solubility of soaps in water; in sufficiently concentrated solutions of common salt, of sodium sulphate, and of caustic alkalis, soaps are insoluble. They are therefore thrown out of their aqueous solutions by adding salt, etc. (*soap-making*). The laurates and ricinoleates are remarkable for the large quantity of salt required to throw them out of their solutions, or, as the term goes, for "salting out."

[1] *Berichte*, 1899, 1594. [2] *Ibid.* 1903, 400.

Stiepel[1] has examined quantitatively the behaviour of sodium salts of caproic, caprylic, capric, lauric, myristic, palmitic, and stearic acids to salt solutions. Whereas a dilute solution of sodium caproate is not "salted" out by a saturated solution of sodium chloride, the laurate is insoluble in a 17 per cent, and the stearate in a 5 per cent solution of sodium chloride.

The commercial soaps, containing potash as alkali, constitute the "soft soaps," and those containing soda the "hard."

The affinities of the fatty acids, which occur in most glycerides, to **caustic soda and potash** are sensibly the same; hence if a mixture of caustic soda and potash be brought into contact with fatty acids, insufficient in quantity to neutralise the total alkali present, a mixture of soda and potash soaps results with excess of the caustic alkalis, the ratio between free caustic soda and potash being approximately the same as that of the combined alkalis. The following table, due to *Alder Wright* and *Thompson*,[2] expresses this clearly; in each experiment for a given amount of fatty acid two equivalents of alkali, one of caustic soda and one of caustic potash, were present:

Fatty Acid.	Percentage of Total Fatty Acid converted into	
	Soda Soap.	Potash Soap.
Pure stearic	51·2	48·8
Pure oleic	50·8	49·2
Crude stearic and oleic (tallow) . .	51·5	48·5
Crude stearic palmitic and oleic (palm oil and tallow)	48·2	51·8
Crude lauric (cocoa nut oil) . .	49·7	50·3
Mean .	50·3	49·7

Practically, in every case half the caustic alkali was present as soap and the other half as uncombined hydroxide (cp. also chap. ii. p. 53). The logical postulate, that a soda soap on treatment with as much caustic potash as is equivalent to the soda present, and conversely, a potash soap with the equivalent of caustic soda, should yield a soap containing half the fatty acid in combination with potash and the other half combined with soda, is thus borne out by the experiments.

The **carbonates** of soda and potash behave in a very different manner from the caustic alkalis. Experiments carried out in a similar fashion to those described in the case of the caustic alkalis proved that the prevailing tendency is towards the formation of potash soap and sodium carbonate, whether potassium carbonate was intermixed with soda soap in proportions equivalent to the basis, or sodium carbonate was intermixed with potash soap; in the latter

[1] *Seifenfabrikant*, 1901, 933. [2] *Journ. Soc. Chem. Ind.* 1885, 626.

case, even when the quantity of sodium carbonate was largely in excess of the amount equivalent to the potash present, only a *comparatively small proportion* of soda soap was formed. The following table, due to the same authors, gives the actual figures obtained :—

Fatty Acid.	Soda Soap fused with CO_3K_2. Percentage of total Fatty Acids present.		Potash Soaps fused with CO_3Na_2. Percentage of total Fatty Acids present.	
	Equivalent to the CO_3K_2 added.	*Actually converted* into Potash Soap.	*Equivalent to* the CO_3Na_2 added.	Actually converted into Soda Soap.
Stearic and oleic (tallow) . .	10·4	8·0		
,, ,,	45·7	34·4		
,, ,,	100·0	97·95	100·0	4·3
,, ,,	104·2	99·00	1000	15·0
Stearic, palmitic, and oleic (palm oil and tallow). . . .	57·2	52·1		
Stearic, palmitic, and oleic (palm oil and tallow). . . .	108·0	90·8	177·0	9·5
Crude lauric (cocoa nut oil) . .	52·8	46·4		
,, ,,	114·8	87·9	197·0	6·2
Crude ricinoleic (castor oil) . .	50·0	48·4		
,, ,,	100·0	93·8	205·0	8·2

The **chlorides** of the alkali-metals behave in the reverse manner, the prevailing tendency being towards the formation of soda soap and potassium chloride; at any rate, these salts are formed in preference to potash soap and sodium chloride when the relative masses are nearly equal. (*Old method of making hard soap from wood ashes.*) On repeating the same operation, the exchange of the metals may become a complete one.

The results obtained by *Alder Wright* and *Thompson* in a series of experiments when using 10 molecules of KCl and 10 molecules of NaCl for 1 molecule of soap consisting of one-half molecule of potash soap and one-half molecule of soda soap are reproduced in the following table :—

Fatty Acid.	*Percentage of Fatty Acid contained*		Molecular Ratio of Soda Soap to Potash Soap.
	As Potash Soap.	As Soda Soap.	
Pure oleic	38·0	62·0	1·63 : 1
Crude ricinoleic (from castor oil)	17·8	82·2	4·6 : 1
Stearic, oleic, and resin (from tallow-resin soap) . .	17·2	82·8	4·8 : 1
Crude lauric (from cocoa nut oil soap)	15·1	85·9	5·7 : 1

By modifying, however, the relative masses, potash soap and sodium chloride can be produced. The experimental proof is given by the figures in the following table, where in the case of columns (*a*) potash soaps dissolved in M molecules of water were salted out by N *molecules of sodium chloride for 1 molecule of soap, and in the* case of columns (*b*) soda soaps dissolved in M molecules of water were salted out by adding N molecules of potassium chloride for 1 molecule of soap.

Fatty Acid.	M	N	(*a*) Potash Soaps salted out with NaCl. Percentage of Fatty Acid in Curd as		(*b*) Soda Soaps salted out with KCl. Percentage of Fatty Acid in Curd as	
			Potash Soap.	Soda Soap.	Potash Soap.	Soda Soap.
Stearic and oleic (from tallow)	100	5	10·5	89·5	79·1	20·9
,, ,,	200	20	5·1	94·9	82·1	17·9
Stearic palmitic and oleic (from palm oil and tallow) . .	200	20	3·8	96·2	95·8	4·2
Crude lauric (from cocoa nut oil)	200	20	5·4	94·6	74·8	25·2

The neutral soaps of the alkali metals are not readily soluble in the organic solvents (with the exception of alcohol) usually employed in analysis, such as ether, petroleum ether, benzene, etc. In the *dry state, the soaps are more soluble in ether and benzene than in* petroleum ether. On shaking aqueous solution of soaps, the soaps dissolve to a slight extent in ether, less so in petroleum ether. Acid soaps behave somewhat differently. Since the solubility of soaps in organic solvents plays an important part in commercial analysis, these points will be considered fully in Chapter IX.

The *ammonia salts* of the fatty acids are obtained by saturating the fatty acids with ammonia. In aqueous solutions dissociation of the ammonia soaps takes place, in a much-increased ratio in comparison with the alkali salts. Aqueous solutions lose ammonia on warming, so that neutral ammonia soaps cannot be prepared on a practical scale. When an ammonia soap is allowed to stand under a bell jar, with a dish of concentrated sulphuric acid, ammonia *is rapidly lost, until the amount left equals one-half of that* present in the neutral soap. The acid soap so obtained usually loses ammonia on further standing, but far less rapidly than the original salts. The acid ammonia salts of stearic and lauric acids appear to be considerably less unstable under these conditions than those of oleic and ricinoleic acids.

With regard to *Lithium* salts, cp. chap. viii. p. 353, and Appendix.

(2) *Salts of the Alkaline Earths and of the Heavy Metals*

The salts falling under this head are best prepared by precipitating aqueous solutions of their ammonium or alkali metal salts with solutions of the acetates.

The salts of the lowest members of the fatty acids are soluble in water, easily forming basic salts which separate out on boiling the solutions.

In the same manner as the solubility of the free acids, starting from butyric acid, decreases with the increase of the number of carbon atoms in the molecule, so likewise the solubility of the salts decreases. The figures for the solubility of the calcium salts given in the following table demonstrate this clearly :—

Calcium Salt of	Soluble in parts of Water.	At Temperature. °C.
Butyric acid . . .	3·5	14
Isovaleric acid . .	4·9	20
Caproic acid . . .	4·4	21-22
Caprylic acid. . .	more than 160·0	·20
Capric acid . . .	large quantity of water	100
Lauric acid . . .	about 2000	100

The barium salts of the volatile acids, as also the lead salts of the volatile acids (*Asbóth*), are to some extent soluble in water, and also in these cases the solubility of the volatile acids themselves corresponds to the solubility of their barium, or lead salts.

Most salts of the lower fatty acids are soluble in alcohol ; those of the higher acids are insoluble in this menstruum.

The lead salts of the higher saturated acids are nearly insoluble in ether, whereas lead oleate, lead linoleate,[1] lead ricinoleate,[1] in short, the lead salts of the most frequently occurring unsaturated acids, are soluble. The lead salt of erucic acid is but sparingly soluble in ether ; the lead salt of iso-oleic acid is stated to be insoluble.

Further information will be found under the headings of the individual acids and in Chapters VIII. and XV.

Behaviour of Fatty Acids with Reagents

The action of sulphuric, nitric, and nitrous acids, further of chlorine, bromine, and iodine on fatty acids, is much the same as the action of these agents on the corresponding glycerides. The action of air on the fatty acids is also similar to the action of air on the glycerides themselves. Thus the fatty acids of the saturated series are not changed under the influence of air at the ordinary temperature. The acids of the unsaturated series, however, such as those to which linolic and linolenic acids belong, absorb oxygen from the atmosphere at the ordinary temperature. The nature of the products so formed has not yet been investigated. The acids belonging to the oleic series absorb oxygen if treated at a somewhat elevated

[1] Linoleate and ricinoleate mean here the salts of the mixed fatty acids from linseed and castor oils respectively.

temperature (cp. "Oleic Acid," p. 105) with the formation of fatty acids insoluble in petroleum ether. I have termed these acids, pending full investigation into their nature, *oxidised acids.*

The higher fatty acids can be freed from adhering water by drying at 100° C. The saturated acids do not absorb oxygen under these conditions; the unsaturated acids, however, must be dried *in vacuo* or in an atmosphere of an indifferent gas.

In the case of some hydroxylated acids, such as ricinoleic acid, polymerisation products are formed. I have shown [1] that in the case of wool wax fatty acids dehydration takes place to a considerable extent at 100° C., no doubt owing to the formation of lactones. The formation of a lactone at the ordinary temperature is exemplified by γ-stearolactone, which is precipitated on decomposing the potassium salt of the γ-hydroxystearic acid with mineral acids.

Anhydrides of the fatty acids are formed readily by heating the latter with acetic anhydride, as I have shown [2] in the cases of capric, lauric, palmitic, stearic, cerotic, and oleic acids.

On heating the higher saturated fatty acids with sodium, magnesium, aluminium, iron, tin, to a temperature of 350° C. there are formed carbonic anhydride, hydrogen, gaseous hydrocarbons, and olefinic hydrocarbons, having 22 to 28 carbon atoms in their molecule. Silver and copper decompose the fatty acids under the same conditions to a very slight extent only. In the case of the lower fatty acids, up to acids of 12 carbon atoms, the reaction is less complicated; ketones are formed, yielding hydrocarbons which stand in near relation to the fatty acids from which they are derived.[3]

I.—Acids of the Acetic Series, $C_nH_{2n}O_2$

Acetic Acid, $C_2H_4O_2 = CH_3 . COOH$

The glyceride of this acid has been found in the seeds of the spindle-tree, *Euonymus europæus*, L. Acetic acid has also been found in Macassar oil. The occurrence of acetic acid as a component of a fat being limited, according to our present knowledge, to these two fats, the properties of this acid need not be detailed here, inasmuch as every text-book of qualitative analysis supplies the necessary information.

Butyric Acid, $C_4H_8O_2 = CH_3 . CH_2 . CH_2 . COOH$

The glyceride of butyric acid occurs in cow butter—as butyrin—to the extent of about 6 per cent.

[1] Lewkowitsch, *Journ. Soc. Chem. Ind.* 1896, 14.
[2] Lewkowitsch, *Proceed. Chem. Soc.* 1890, 91.
[3] Hébert, *Bull. de la Soc. Chim.* 1903, 316.

Butyric acid at the ordinary temperature is a colourless liquid. When freshly distilled its odour resembles that of acetic acid; diluted with water it has a smell resembling that of rancid butter. It crystallises at $-19°$ C.; the crystals melt at $-6·5°$ C. The acid boils under ordinary pressure at 162·3° C., under 758 mm. pressure 163°-164° C. (*Scheij*), and has the specific gravity 0·9746 at 0° C.; 0·958 at 14° C.; 0·9590 at $\frac{20°}{4°}$ C., and 0·8141 at $\frac{161·5°}{4°}$ C. The refractive index n_D^{20} is 1·39906.

Butyric acid is miscible with water, alcohol, and ether in all proportions; it separates from its aqueous solution in the form of oily drops on adding calcium chloride or common salt.

Solutions of butyric acid have a sour, burning taste; they redden tincture of litmus, and discharge the pink colour of slightly alkaline solutions containing phenolphthalein. Methylorange turns red in solutions of butyric acid free from butyrates (cp. p. 73).

On distilling a dilute aqueous solution of butyric acid it all passes over into the distillate. If the solution is too weak it is preferable to neutralise with caustic soda and concentrate by evaporation. The concentrated solution is then acidified by means of dilute sulphuric acid and distilled.

On warming an alcoholic solution of butyric acid with concentrated sulphuric acid, ethyl butyrate is formed, the smallest quantity of which may be recognised by its pleasant odour, resembling that of pine-apples. Butyric acid is detected by means of this reaction in dilute solutions *by neutralising with caustic soda, evaporating to dryness,* and warming the residue gently with alcohol and sulphuric acid. In fats containing butyrin, it is rapidly detected by saponifying with strong alcohol and an amount of caustic potash insufficient to effect complete saponification, ethyl butyrate being formed. (Qualitative detection of butter fat.)

The metallic salts of butyric acid are—with the exception of the silver, mercurous, and lead salts—*easily* soluble in water; the salts of the alkalis are deliquescent.

Calcium butyrate, $Ca(C_4H_7O_2)_2 + H_2O$, is remarkable on account *of its solubility decreasing with the increase of temperature.* At 14° C. the saturated solution contains 1 part of the salt dissolved in 3½ parts of water. On warming to 30° C. a precipitate is obtained, and on boiling, the salt separates, nearly completely re-dissolving on cooling. The calcium salt is soluble in alcohol.

Barium butyrate, $Ba(C_4H_7O_2) + 4H_2O$. 100 parts of water dissolve from 0° to 40° C.: 37·5 parts of the anhydrous salt, and from 40° to 82° C.: 35·9 parts. 100 parts of absolute alcohol dissolve 0·126 parts of the anhydrous salt.[1]

Silver butyrate, $AgC_4H_7O_2$, dissolves in 200 parts of water at 14° C. It crystallises in needles or monoclinic prisms according to the concentration.

[1] With regard to the barium salt, cp. Wilcox, *Proceed. Chem. Soc.* 1895, 202.

Isovaleric Acid, $C_5H_{10}O_2 = (CH_3)_2 . CH . CH_2 . COOH$

This acid occurs as a glyceride—triisovalerin—in porpoise and dolphin oils, the blubber oils from *Delphinus phocæna* and *Delphinus globiceps*. *Chevreul*, who discovered the acid when examining dolphin oil, termed it phocenic acid.

The odour of isovaleric acid is like that of valerian root or putrid cheese.

The acid is a colourless liquid; its boiling point is 173·7° C. at 760 mm. pressure; 99·2° C. under 45·9 mm. pressure; and 72·4° C. under 10·5 mm. pressure. *It solidifies at* −57° C. and melts at −51° C.;[1] its specific gravity is 0·9467 at 0° C., 0·931 at 20° C. It dissolves in 23·6 parts of water at 20° C.; it is thrown up from this solution by calcium chloride.

Caproic Acid, $C_6H_{12}O_2 = CH_3 . CH . CH_2 . CH_2 . CH_2 . COOH$

Caproic acid occurs, in combination with glycerol, as the glyceride caproin, in cow butter and in cocoa nut oil. The acid is not miscible with water, although to some extent soluble in it. Its melting point is −8° C. (*Scheij*); it boils at 202-203° C. at 770 mm. pressure. The specific gravity is 0·924 at $\frac{20°}{4°}$ C.; the refractive index $n_D^{20} = 1·41635$. *Its odour is like that of sweat.*

The calcium salt crystallises with one molecule of water in laminæ ($[C_6H_{11}O_2]_2Ca + H_2O$); 100 parts of water dissolve 4·4 parts of the anhydrous salt at 21°-22° C. The barium salt crystallises *with 2 molecules of water* ($(C_6H_{11}O_2)_2Ba + 2H_2O$); *100 parts of water dis*solve 11·1 parts of anhydrous salt at 10·5° C. The zinc salt is precipitated as a crystalline powder of the composition $(C_6H_{11}O_2)_2Zn + H_2O$ on pouring caproic acid into a zinc acetate solution. (Difference from butyric and valeric acids.) 100 parts of water dissolve 1·03 parts *of the anhydrous salt at 34·5° C.*

Caprylic Acid, $C_8H_{16}O_2 = CH_3 . (CH_2)_6 . COOH$

Caprylic acid exists as a glyceride in cow butter, in human fat, and notably in cocoa nut oil. Liquid at the ordinary temperature, it crystallises in laminæ on cooling to 12° C., melting at 16·5° C.; it boils at 236°-237° C. under 761 mm. pressure, and from 123·5°-124·3° C. under 10 mm. pressure. Its specific gravity is 0·9270 at 0°, and 0·9100 at $\frac{20°}{4°}$ C. Its refractive index is $n_D^{20} = 1·42825$. One part dissolves in 400 parts of boiling water; on cooling it separates out nearly completely. The acid has an intense odour of sweat.

The barium salt $(C_8H_{15}O_2)_2Ba$ crystallises in laminæ; 100 parts of water dissolve 0·619 parts at 20° C. The lead salt $(C_8H_{15}O_2)_2Pb$ crystallises from alcohol in laminæ, melting at 83·5°-84·5° C.

[1] Massol, *Journ. Soc. Chem. Ind.* 1895, 828.

Capric Acid, $C_{10}H_{20}O_2 = CH_3 . (CH_2)_8 . COOH$

The butter fat of the cow and goat contains this acid combined with glycerol as the glyceride caprin; it also occurs in the fat from *Lindera Benzoin*; the glyceride is also found in cocoa nut oil in association with the glycerides of the two preceding acids. As a potassium salt the acid occurs in wool yolk.

Capric acid crystallises in fine needles, having the melting point 31·3°-31·4° C., and boiling point 268°-270° C. under ordinary pressure; 199·5°-200° C. under 100 mm.; 153°-154° C. under 13 mm. pressure.

The specific gravity of the acid at 37° C. is 0·930; at $\frac{40°}{4°}$ = 0·8858. Its refractive index is $n_D^{40} = 1·42855$.

Nearly insoluble in cold water, it dissolves in about 1000 parts of boiling water. The acid has a goat-like smell, which becomes more distinct at the temperature of its melting point. Of the caprates, the salts of the alkalis only are easily soluble in water. The barium salt is nearly insoluble in cold water, and very sparingly soluble in boiling water. It crystallises from the latter in laminæ. The salt is easily soluble in boiling alcohol.

Lauric Acid, $C_{12}H_{24}O_2$

Lauric acid is found as a glyceride in considerable quantities in tangkallak fat, the fat from the fruit of *Cylicodaphne (Litsæa) sebifera*, and in laurel oil; cocoa nut oil, pichurim beans, spermaceti, and the fat from *Lindera Benzoin* also contain notable proportions of laurin. The fatty acid contained in the nuts of the Californian bay-tree, *Umbellularia californica* (formerly described as umbellulic acid), is true lauric acid.

The acid is solid at the ordinary temperature, and crystallises from alcohol in needles, melting at 43·6° C. Lauric acid is the first acid of the acetic series that cannot be distilled at ordinary pressure without undergoing slight decomposition. Its boiling point is 225° C. at 100 mm., 176° C. at 15 mm., 102° C. *in vacuo*. The specific gravity is 0·883 at $\frac{20°}{4°}$ C., 0·875 at $\frac{43·6°}{4°}$ C., and 0·8642 at $\frac{60°}{4°}$ C. Its refractive index $n_D^{20} = 1·42665$, $n_D^{70} = 1·4236$ (*Partheil* and *Ferié*).

Lauric acid is slightly soluble in large quantities of boiling water; on distilling the aqueous solution it passes over to an appreciable extent with the vapours. It has been repeatedly pointed out above that lauric acid occupies an intermediate position between the soluble and the insoluble fatty acids. Thus the laurates of the alkali-metals differ from the corresponding salts of the higher fatty acids in that they require large quantities of salt for "salting out." (Cocoa nut soaps, marine soaps.)

The *solubilities of a number of metallic salts of lauric acid*

in water and alcohol are given in the following table due to *Oudemans* :—

Name of Salt.	Formula.	1000 parts of Water dissolve		1000 parts of Alcohol dissolve	
		At the Boiling Point.	At 15° C.	At the Boiling Point.	At 15° C.
Magnesium laurate	$Mg\bar{A}_2 + 3H_2O$	0·411	0·230	126·0	15·25
Calcium laurate	$Ca\bar{A}_2 + H_2O$	0·547	0·039	22·02	0·719
Strontium laurate	$Sr\bar{A}_2 + H_2O$	0·360	0·272	3·59	9·598
Barium laurate	$Ba\bar{A}_2$	0·698	0·054	1·009	0·187
Zinc laurate	$Zn\bar{A}_2 + H_2O$ (?)	0·189	0·103	8·78	0·134
Lead laurate	$Pb\bar{A}_2$	0·011	...	2·35	0·047
Manganese laurate	$Mn\bar{A}_2 + xH_2O$	0·401	0·011	3·82	0·481
Cobalt laurate	$Co\bar{A}_2 + H_2O$	0·376	0·072	18·01	0·174
Nickel laurate	$Ni\bar{A}_2 + H_2O$ or $3H_2O$	0·390	0·197	6·68	0·640
Copper laurate	$Cu\bar{A}_2$	0·029	0·023	6·53	0·775
Silver laurate	$Ag\bar{A}$	0·405	0·001	0·824	0·323
Lithium laurate	$Li\bar{A}$	see	Appendix		

Ethyl ester, see Appendix.

Ficocerylic Acid, $C_{13}H_{26}O_2$ [1]

Ficocerylic acid is the acid constituent of gondang wax; it melts at 57° C.

Myristic Acid, $C_{14}H_{28}O_2$

The fat, obtained from the seeds of *Virola venezuelensis*,[2] consists of almost pure myristin, the glyceride of myristic acid. The acid further occurs in considerable quantities in nutmeg butter (from *Myristica moschata*); in otoba fat (from *Myristica otoba*); in dika oil, and to a smaller extent also in cocoa nut oil, lard, butter fat, wool wax, and in the wax of cochineal. It has also been found in the form of cetyl myristate in spermaceti. In very small quantities it has been recently detected in the gall of oxen.

Myristic acid crystallises in laminæ of the melting point 53·8° C., and boiling point 250·5° C. at 100 mm., 196·5° C. at 15 mm., 121°-122° C. *in vacuo*. The specific gravity is 0·8622 at $\frac{53·8°}{4°}$ C.; 0·8584 at $\frac{60°}{4°}$ C.; its refractive index $n_D^{60} = 1·43075$, $n_D^{76·5} = 1·4248$.

The acid is completely insoluble in water; when boiled with water very slight quantities of the acid are carried away with the vapour. It dissolves with difficulty in cold alcohol and ether.

The barium salt forms a crystalline powder, very sparingly soluble in water and alcohol. Lithium salt, see Appendix.

The ethyl ester of myristic acid solidifies at 10·5°-11·5° C. (see App.).

[1] Greshoff and Sack, *Rec. des trav. Chim. de Pays-Bas*, 1901, 65.
[2] Thoms and Mannich, *Ber. d. d. pharm. Ges.* 1901, 264.

ISOCETIC ACID, $C_{15}H_{30}O_2$

The glyceride of this acid is stated by *Bouis* to occur in the oil from the seeds of *Jatropha curcas* (purging nut oil, curcas oil). The acid crystallises in laminæ, having the melting point 55° C. The existence of this acid is somewhat doubtful.

PALMITIC ACID, $C_{16}H_{32}O_2$

Palmitic acid occurs as a glyceride—palmitin—in most vegetable and animal fats; and notably in large quantities in palm oil, vegetable tallow (from *Stillingia sebifera*), and Japan wax. It occurs also in spermaceti as cetyl palmitate, in beeswax as myricyl palmitate, and in opium wax as ceryl palmitate.

The preparation of palmitic acid from oleic acid by melting the latter with caustic alkali is important from a commercial[1] point of view. *The reaction is generally stated to take place according to the* following equation:—

$$C_{18}H_{34}O_2 + 2KOH = KC_{16}H_{31}O_2 + KC_2H_3O_2 + H_2,$$

but it should be noted that oxalic acid is formed in greater quantity than acetic acid, which latter is obtained in extremely small quantities.[2]

Pure palmitic acid forms tufts of finely crystallised needles; the melted acid solidifies on cooling to a nacreous, scaly, crystalline mass. The acid is free from smell or taste. The melting point is 62·62° C.; the solidifying point of a carefully purified specimen is given by *de Visser*[3] as 62·618° C. It boils between 339° and 356° C. with slight decomposition; it distils unchanged under a pressure of 100 mm. at 271·5° C., under a pressure of 15 mm. at 215° C., and *in vacuo* at 138°-139° C. The specific gravity of the acid is 0·8527 at $\frac{62°}{4°}$ C.; 0·8412 at $\frac{80°}{4°}$ C.; its refractive index $n_D^{74.5} = 1.4284$, $n_D^{80} = 1.42693$.

Palmitic acid is not readily soluble in cold alcohol; 100 c.c. of (methylated) alcohol, specific gravity 0·8183 (containing 94·4 per cent of alcohol by volume), were found to dissolve the following quantities, after the solutions had been kept the number of hours stated at 0° C.:[4]—

Hours.	Grms.
	1·298-1·320
36	1·244
60	1·211
84	1·134
108	1·086
132	1·044
156	1·028

[1] Lewkowitsch, *Journ. Soc. Chem. Ind.* 1897, 390.

[2] Edmed, *Journ. Chem. Soc.* 1898, 633.

[3] *Journ. Soc. Chem. Ind.* 1898, 853.

[4] Hehner and Mitchell, *Analyst*, 1896, 323. Kreis and Hafner, however, state that 100 c.c. of alcohol containing 95 per cent by volume retain in solution at 0° 0·56 grm. (*Berichte*, 1903, 2769).

100 parts of absolute alcohol dissolve at 19·5° C. 9·32 parts only. The acid dissolves very readily in boiling alcohol, and therefore this menstruum is conveniently used for purifying palmitic acid. Petroleum ether does not dissolve it very readily.

Dilute acids have no action on palmitic acid; it dissolves, however, in concentrated sulphuric acid. On diluting this solution with water, the palmitic acid separates unchanged. Boiling concentrated nitric acid attacks it very slowly. On oxidising it in alkaline solution by means of potassium permanganate, acetic, butyric, caproic, oxalic, succinic, adipic, and acids of the formulæ $C_5H_9O_3$ and $C_{16}H_{32}O_4$ are formed. Concentrated solutions of permanganate yield lower members of the fatty acid series than dilute solutions.

The metallic salts of palmitic acid resemble very much those of stearic acid (see p. 95), but they possess a somewhat greater solubility. The behaviour of sodium palmitate with water has been described above (p. 77). 100 c.c. of 95 per cent alcohol dissolve 1·136 grms. of potassium palmitate at 22° C. (*Geitel* and *v. d. Want*). The silver palmitate can be obtained in a crystalline form by adding an alcoholic solution of silver nitrate to an alcoholic solution of ammonium palmitate; silver palmitate separates from the solution in the shape of small, lustrous laminæ. Lead palmitate is almost insoluble in absolute ether, 50 c.c. of the latter dissolving 0·0092 grm. of the lead salt. Lithium palmitate, see Appendix.

The solubility of a number of palmitates in absolute alcohol is given in the following table:—

100 Parts of Absolute Alcohol dissolve		
	at 20° C.	at boiling point.
Calcium palmitate	0·0103 parts	...
Barium palmitate	0·0035 ,,	0·0128 parts
Magnesium palmitate	0·0146 ,,	0·0197 ,,
	at 19° C.	
Lead palmitate	0·0007 ,,	
	at 21° C.	
Lead palmitate, freshly precipitated	0·0033 ,,	

A quantitative determination of palmitic acid may be effected by precipitating it from the solution of palmitates by means of hydrochloric acid, washing the precipitate with water, dissolving it in absolute alcohol, evaporating to dryness, and finally drying in a desiccator over sulphuric acid.

The methyl-, and ethyl-esters melt at 28° C. and 24·2° C. respectively (see Appendix).

DATURIC ACID, $C_{17}H_{34}O_2$

The glyceride of daturic acid has been found in datura oil, the oil from the seeds of *Datura Stramonium* (thorn-apple).[1] The

[1] Gérard, *Journ. Soc. Chem. Ind.* 1890, 1137; Holde, *Mitth. d. Königl. Techn. Versuchsanst.* 1902, 66.

acid dissolves more easily in cold alcohol than palmitic acid, and crystallises from it in fine needles, melting point 54·5° C. *Nördlinger*[1] claims to have found the same or an isomeric acid amongst the solid fatty acids of palm oil to the amount of 1 per cent; this acid melts at 57° C., and boils between 223° and 225° C. under a pressure of 15 mm. The magnesium salt crystallises in microscopic needles, of the melting point 135°-140° C.

The methyl-, and ethyl-esters melt at 30° C. and 26·7° C. respectively.

MARGARIC ACID is an obsolete (commercial) term for a mixture of palmitic and stearic acids, for which, in older text-books, the formula $C_{17}H_{34}O_2$ is assumed. (The butter substitute "margarine" derives its name from this acid.) This mixture of palmitic and stearic acid has a constant melting point, and the constituents cannot be separated by mere re-crystallisation of the mixture. Synthetically a margaric acid of the formula $C_{17}H_{34}O_2$ has been prepared by *Krafft*; this acid melts at 59·8° C. and boils under a pressure of 100 mm. at 227° C. A mixture of daturic and this synthetical margaric acid in molecular proportions melted at 53·5°-54·5° C.[2]

STEARIC ACID, $C_{18}H_{36}O_2$

Stearic acid occurs largely as a glyceride—stearin—in many natural fats, especially in the harder ones, such as tallow. The higher the melting point of a fat the greater will, as a rule, be found its percentage of stearin.

Pure stearic acid forms white, nacreous laminæ melting at 69·32° C. to a perfectly colourless liquid which, on cooling, solidifies to a crystalline translucent mass at 69·3° C. This melting point has been ascertained by *de Visser* for a very carefully purified specimen of acid. (*Saytzeff* gives 71° to 71·5° C. as the melting point. *Fritzweiler*, who prepared a pure stearic acid from cacao butter oleodistearin, gives the melting point 70° C.) The acid boils at about 360° C. under ordinary pressure with slight decomposition; under a partial vacuum it distils, however, unchanged. The boiling point for 100 mm. pressure is 291° C., for 15 mm. 232° C., and *in vacuo* the acid boils at 154·5°-155·5° C. The acid may also be distilled in a current of steam without fear of partial destruction.

The specific gravity of stearic acid is 0·8454 at $\frac{69 \cdot 2^\circ}{4^\circ}$ C., and 0·8386 at $\frac{80^\circ}{4^\circ}$ C. At 11° C. its specific gravity is that of water; at more elevated temperatures it floats on water, expanding more quickly than the latter. The refractive index is $n_D^{80} = 1 \cdot 43003$.

Like palmitic acid it possesses neither smell nor taste, is greasy to the touch, and produces a grease-spot on paper.

Insoluble in water, it dissolves easily in hot alcohol. It is less

[1] *Journ. Soc. Chem. Ind.* 1892, 444.
[2] Holde, *Mitth. d. Königl. Techn. Versuchs.* 1902, 62.

soluble in absolute alcohol than palmitic acid, one part of stearic acid requiring 40 parts of this solvent. 100 c.c. alcohol (methylated), of specific gravity 0·8183 (containing 94·4 per cent of alcohol by volume), dissolve at 0° C. 0·155 to 0·158 grm. after 12 hours' standing, and 0·145 to 0·153 grm. after 36 hours' standing.[1] Stearic acid dissolves easily in ether; at 23° C. 1 part of benzene dissolves 0·22 parts of the acid, and 1 part of carbon bisulphide 0·3 parts. On oxidising stearic acid with potassium permanganate *Carette* obtained dibasic acids (succinic, adipic). *Marie*[2] has found amongst the products of oxidation normal valeric acid (not isovaleric acid, contrary to previous statements[3]).

Stearates of the Alkali-Metals.—These stearates are prepared by adding stearic acid to aqueous solutions of potassium or sodium carbonates, whereby carbonic acid is expelled. A better method, however, is to add the boiling aqueous solution of the carbonates to an alcoholic solution of stearic acid, and to evaporate to dryness; the excess of the carbonate is then removed by exhaustion of the residue with alcohol. From the alcoholic solution the salts deposit on cooling. The alkali salts crystallise when quite pure.

In ether, petroleum ether, carbon bisulphide, and chloroform, the stearates of the alkali-metals are insoluble (difference from oleic acid). Lithium stearate, see Appendix.

Potassium stearate, $KC_{18}H_{35}O_2$, forms crystals having a greasy lustre; they dissolve in 6·6 parts of boiling alcohol. On diluting the hot aqueous solution of the potassium stearate with a large proportion of water, pearly laminæ of an acid stearate separate, having the formula $KC_{18}H_{35}O_2 . C_{18}H_{36}O_2$.

Sodium stearate, $NaC_{18}H_{35}O_2$, resembles very much in its properties the potassium salt; the crystals form lustrous laminæ. The acid salt has the formula $NaC_{18}H_{35}O_2 . C_{18}H_{36}O_2$.

Ammonium stearate, $(NH_4)C_{18}H_{35}O_2$, on being warmed in aqueous solution loses part of its ammonia, and is converted into the acid salt. The same change takes place when the ammonia soap is allowed to stand over concentrated sulphuric acid in a desiccator.

The other metallic salts of stearic acid are best obtained by double decomposition from sodium stearate, or, better still, by precipitating alcoholic solutions of stearic acid with solutions of the acetates of the metals. The stearates thus obtained are insoluble in water.

Calcium, strontium, and *barium stearates* form crystalline precipitates, practically insoluble in alcohol. The *magnesium* salt crystallises in microscopical laminæ; it is nearly insoluble in cold alcohol, but sufficiently soluble in boiling alcohol to allow its being crystallised from the solution.

The stearates of the heavy metals, such as the *silver*, *copper*, and the

[1] Hehner and Mitchell, *Analyst*, 1896, 323.

[2] *Journ. Soc. Chem. Ind.* 1896, 362.

[3] The statement made by Fleurent (*Journ. Soc. Chem. Ind.* 1898, 852) that stearic acid heated in thin layers to 120° C. with free admission of air is converted into an intermediate liquid form (in the cold) before definitely assuming the form of linoxyn, requires confirmation.

lead salts, are amorphous; the last-named salt melts at 115°-116° C. without undergoing decomposition. The *lead* salt is very sparingly soluble in ether (difference from oleic acid), and less still in petroleum ether (*Twitchell*). 50 c.c. of absolute ether dissolve 0·0074 grm. of lead stearate (*Lidoff*). In hot benzene lead stearate dissolves, but separates almost completely on cooling to 8°-12° C.

The insoluble salts of stearic acid are partly decomposed on washing with water. Thus barium stearate loses thereby barium oxide, and with the undissociated residue there remains some free stearic acid which can be extracted by alcohol. This is of importance for the quantitative determination of stearic acid (also of palmitic and oleic acids), as has been shown by *Chittenden* and *Smith*. In accurate estimations the salts cannot be employed; the free acids must be separated and weighed as such.

The methyl-, and ethyl-esters of stearic acid melt at 38° C. and 33·7° C. respectively (see Appendix).

ARACHIDIC ACID, $C_{20}H_{40}O_2$

The glyceride of arachidic acid has been found in very small quantities in cow butter. It occurs in larger quantities in arachis oil and in Rambutan tallow, the fat from the seeds of *Nephelium lappaceum*, L., in smaller quantities in rape oil, cacao butter, macassar oil, elderberry oil, etc. Arachidic acid has also been obtained from a fatty acid occurring in grape-seed oil (erucic acid?) on heating with melted caustic potash. Arachidic acid crystallises in small, lustrous scales having the melting point 77° C. The acid is soluble in cold alcohol with great difficulty, but dissolves easily in boiling alcohol. Part of the acid is stated to become converted into ethyl arachidate during this operation;[1] to avoid loss in recrystallising, the acid should, therefore, only be boiled until the arachidic acid has passed into solution; 100 parts of 90 per cent alcohol dissolve at 15° C. 0·022 parts of arachidic acid, and at 20° C. 0·045 parts. The acid is therefore much less readily soluble than stearic acid. It dissolves readily in ether, chloroform, ligroin, and benzene.

The metallic salts of arachidic acid are very similar to the stearates. The copper salt crystallises from alcohol in needles, the silver salt in prisms.

The methyl-, and ethyl-esters melt at 54·5° C. and 50° C. respectively. The latter boils at 284°-286° C. under 100 mm. pressure.

BEHENIC ACID, $C_{22}H_{44}O_2$

The oil of ben (or behen), expressed from the seeds of *Moringa oleïfera*, contains the glyceride of this fatty acid. The melting point of behenic acid is 80°-82° C., *its solidifying point* 79°-76° C.[2] Synthetical behenic acid from erucic acid[3] melts at 83°-84° C., and

[1] This behaviour has not been observed in the case of palmitic and stearic acids.
[2] *Journ. für prakt. Chemie*, 1894, 61. [3] Talanzeff, *ibid.* 1895, 50; 71-73.

solidifies at 79°-77° C. The acid crystallises in needles; it is less soluble in alcohol than in ether. 100 parts of alcohol dissolve 0·102 grms. at 17° C., and 100 parts of ether at 16° C. 0·1922 grm. of acid. The ethyl ester melts at 48°-49° C.

LIGNOCERIC ACID, $C_{24}H_{48}O_2$

The glyceride of this acid has been shown to occur in arachis oil, in association with arachidic acid. The melting point of lignoceric acid is 80·5° C.; the melted acid solidifies on cooling into a mass possessing radiated structure; when cold, this mass becomes brittle. The acid crystallises from alcohol in white flocks of silky lustre; on pressing between filter-paper, they become scaly and show nacreous lustre. Lignoceric acid is very sparingly soluble in cold alcohol but dissolves readily in benzene, ether, and carbon bisulphide. The copper salt is hardly soluble in alcohol or ether, but dissolves in hot benzene.

The methyl-, and ethyl-esters melt at 56·5°-57° C. and 55° C. respectively.

CARNAÜBIC ACID, $C_{24}H_{48}O_2$

This isomeride of lignoceric acid occurs as an ester, combined with higher alcohols, in carnaüba wax; it has been also found in wool wax.[1] Carnaübic acid is obtained on oxidising carnaübyl alcohol with chromic acid in glacial acetic acid solution. It is sparingly soluble in cold methyl alcohol, but easily soluble in boiling alcohol, ether, benzene, petroleum ether, and glacial acetic acid. Its melting point is 72·5° C.; its solidifying point 69°-67° C. The ammonium salt is stated to be insoluble in water and alcohol; the potassium salt is sparingly soluble in these menstrua in the cold, more readily so at higher temperatures. The lead salt melts at 110°-111° C.

PISANGCERYLIC ACID, $C_{24}H_{48}O_2$

This isomeride of lignoceric acid occurs as an ester of pisangceryl alcohol in pisang wax. It melts at 71° C. It is likely that this acid is identical with carnaübic acid.

HYÆNIC ACID, $C_{25}H_{50}O_2$

The glyceride of this acid has been stated to occur in the anal glandular pouches of the striped hyæna. Its melting point lies between 77° and 78° C. The existence of this acid is doubtful. The calcium salt is a crystalline powder melting at 85°-90° C.

CEROTIC ACID, $C_{26}H_{52}O_2$

Cerotic acid occurs in the free state in beeswax and in carnaüba wax. It has been shown to be present in insect (Chinese) wax,

[1] *Journ. Soc. Chem. Ind.* 1896, 460; *Berichte*, 29, 618; 2892.

opium wax, and in wool wax in combination with ceryl alcohol, as cerylic cerotate. As a glyceride it is stated to occur in the fatty oil from *Aspidium filix mas.*

Crude cerotic acid is prepared from beeswax by exhausting it with boiling alcohol; it is a wax-like mass, melting between 78° and 82° C. It separates from its alcoholic solution on cooling in thin, straight or curved needles. The separation is so complete in the course of a few hours, that the addition of water to the filtrate produces only a milky turbidity but no precipitate. This constitutes an essential difference from palmitic and stearic acids. *Marie* states that the crystals deposited from alcohol vary according to the purity of the acid. Pure *cerotic acid crystallises from alcohol in stellate, microscopic needles*, melting point 77·8° C. (corr.); from benzene in dense laminæ, and from ether in tabular masses consisting of large aggregated needles. (If the acid contains neutral substances, the crystals deposited from alcohol form a gelatinous mass consisting of microscopic needles, and containing a large proportion of alcohol; if the impurity is melissic acid, short granular crystals separate.) The specific gravity of cerotic acid is 0·8359 at $\frac{79°}{4°}$ C.

On boiling with sodium carbonate or dilute aqueous caustic soda, the acid does not pass into solution; it dissolves, however, in boiling alcoholic potash. On cooling, the potassium cerotate solidifies to a mucilaginous mass (*Barfoed*).

Cerotic acid can be estimated volumetrically in its alcoholic solution by caustic potash, with phenolphthalein as an indicator. By using this method[1] for the determination of the molecular weight (cp. p. 332), the uncertainty which attached for a long time to the *composition of cerotic acid has been definitely removed in favour of* the formula $C_{26}H_{52}O_2$.

Schalfejeff[2] had thrown some doubt on the existence of an acid of the composition of cerotic acid, but its existence was confirmed by *Nafzger*,[3] by *Zatzek*,[4] and by *Marie*.[5] Yet the ultimate composition of cerotic acid has not yet been definitely ascertained by these chemists, since the elementary analyses of cerotic acid and its esters agree with either of the formulæ $C_{26}H_{52}O_2$, or $C_{25}H_{50}O_2$.[6] No definite information can be gained from ultimate analysis, the differences in the percentage compositions approximating too closely the errors of analysis, as a glance at the following table will show:—

	C	H	O
	Per cent.	Per cent.	Per cent.
$C_{27}H_{54}O_2$.	79·02	13·17	7·81
$C_{26}H_{52}O_2$.	78·80	13·12	8·08
$C_{25}H_{50}O_2$.	78·53	13·09	8·38

[1] *Proc. Chem. Soc.* 1890, 92.
[2] *Berichte*, 9. 278; 1688.
[3] *Annalen*, 224. 256.
[4] *Berichte*, 15. 2625.
[5] *Journ. Soc. Chem. Ind.* 1894, 1207; 1895, 599.
[6] *Journ. Soc. Chem. Ind.* 1896, 362.

The differences in the neutralisation values of acids having the three formulæ in question are larger than the errors inherent in the method,[1] as shown by the following table:—

	Molecular Weight.	Neutralisation Value.
$C_{27}H_{54}O_2$ . . .	410	136·8
$C_{26}H_{52}O_2$ . . .	396	141·7
$C_{25}H_{50}O_2$ . . .	382	146·8

Since *Lewkowitsch*[2] found the neutralisation value of pure cerotic acid from beeswax = 142·1, and *Henriques*,[3] later on, that of cerotic acid from Chinese wax = 141·4, $C_{26}H_{52}O_2$ must be accepted as the true formula of cerotic acid.

The sodium and potassium salts are easily soluble in boiling water.

A one per cent solution of pure cerotic acid in boiling alcohol gives no precipitate with magnesium acetate; the salt separates out only after cooling to 50° C. However, if the cerotic acid contain melissic acid, an immediate precipitate is obtained. Magnesium cerotate melts at 174°-176° C. The lead salt is insoluble in water, alcohol, and ether. It dissolves in hot benzene and crystallises from this solution in needles. The salt melts at 112·5°-113·5° C. The methyl-, and ceryl-esters melt at 60° C. and at 59°-60° C. respectively. The ceryl ester has been described already (p. 32).

Melissic Acid, $C_{30}H_{60}O_2$

Melissic acid occurs, also in the free state, in beeswax. It crystallises in scales possessing silky lustre, and melting at 91° C. *Schwalb*,[4] has prepared, from beeswax-myricyl alcohol, a melissic acid crystallising from petroleum ether in small, fine needles, to which he ascribes the formula $C_{31}H_{62}O_2$, and the melting point 88·5°-89° C. The melissic acid, $C_{30}H_{60}O_2$, is readily soluble in warm alcohol, chloroform, carbon bisulphide, and petroleum ether, but sparingly soluble in ether and methyl alcohol. The lead salt is insoluble in alcohol and ether; soluble in boiling chloroform. It crystallises from toluene in needles, melting at 118°-119° C.

The methyl-, and ethyl-esters melt at 74·5° C. and 73° C. respectively. The myricyl ester has been described already.

Psyllostearylic Acid, $C_{33}H_{66}O_2$

This acid occurs in Psyllawax combined with psyllostearylic alcohol as a wax. The acid is easily soluble in alcohol, less soluble in petroleum ether and in common ether. The crystals melt at 94°-95° C.

[1] *Proc. Chem. Soc.* 1890, 92.
[2] Cp. *Jahrb. f. Chemie*, 7, 369.
[3] *Zeit. f. ang. Chem.* 1897, 366.
[4] *Annalen*, 235, 135.

II.—Acids of the Oleic Series, $C_nH_{2n-2}O_2$

The acids belonging to the oleic (or acrylic series, from acrylic acid, its lowest member) are unsaturated compounds, and possess therefore the property of absorbing chlorine, bromine, iodine, and the hydrogen acids of these halogens. They assimilate two atoms of the halogens, or one molecule of the halogen acids, being converted thereby into derivatives of acids belonging to the acetic series. The lower unsaturated acids also take up hydrogen when acted upon with sodium amalgam in alkaline solution, and thus become, in a direct way, reduced to acids of the saturated series, but the higher acids behave differently. Thus oleic acid does not take up hydrogen,[1] and cannot be converted into stearic acid by this reaction; stearic acid is, however, obtained from oleic acid on treating it with fuming hydriodic acid, in presence of phosphorus, at a temperature of 200°-210° C. The following equation illustrates the chemical change, which, however, is by no means a quantitative one:—

$$C_{18}H_{34}O_2 + 2HI = C_{18}H_{36}O_2 + I_2.$$

The lower members of this series volatilise without undergoing decomposition, and are miscible with water in every proportion. With the increase of the number of carbon atoms the boiling points rise, and the solubility in water decreases. The specific gravity also diminishes.

The higher acids of this series cannot be distilled under ordinary pressure, but in a current of superheated steam or *in vacuo* they pass over unchanged.

Some of the higher acids, notably oleic and erucic acids, when treated with a small quantity of nitrous acid at the ordinary temperature, or with sulphurous acid or bisulphites at high temperatures and under pressure, are changed into crystallisable isomerides.

A characteristic property of the lead salts of the higher acids is their solubility in ether; this property is made use of in the separation of the higher acids of this series from the corresponding acids of the acetic series. Elaïdic acid, however, simulates, also as regards the solubility of its lead salts in ether, stearic acid (cp. p. 80); lead iso-oleate is less readily soluble in ether than the oleate; the lead salt of erucic acid is sparingly soluble in cold ether.

The unsaturated acids are far more readily soluble in alcohol than the saturated acids having the same number of carbon atoms.

If oxidised by means of a dilute solution of potassium permanganate in alkaline solution, the unsaturated acids are converted into hydroxylated acids (see p. 121). When melted with caustic alkalis they are broken up into two lower acids; thus oleic acid yields palmitic and acetic acids (cp., however, p. 92).

[1] Lewkowitsch, *Journ. Soc. Chem. Ind.* 1897, 390.

Tiglic Acid, $C_5H_8O_2 = CH_3 . CH : C(CH_3) . COOH$

The glyceride of tiglic acid occurs in croton oil. The acid, an isomeride of angelic acid, crystallises in triclinic columns, melting at 64·5° C., and boiling at 198·5° C. under ordinary pressure. The specific gravity at 76° C. is 0·9641. Sodium amalgam has no effect on the acid. On melting it with caustic potash, acetic and propionic acids are produced. On oxidising with potassium permanganate, carbonic acid, acetaldehyde, acetic acid, and dihydroxytiglic (tigliceric) acid are formed.

Fittig's[1] researches prove that tiglic acid occurs in croton oil as such, and is not formed from angelic acid under the influence of the caustic soda used in saponifying the oil (as has been assumed repeatedly), for on prolonged boiling of angelic acid with caustic soda hardly 5 per cent of tiglic acid was obtained.

The calcium salt—$(C_5H_7O_2)Ca + 3H_2O$—is more readily soluble in boiling water than angelic acid. 100 parts of water dissolve at 170° C. 6·05 parts of the anhydrous salt. The ethyl-ester boils at 156° C.

Acids $C_{12}H_{22}O_2$ and $C_{14}H_{26}O_2$

These acids are said to occur in combination with glycerol in the fat of cochineal.[2]

Hypogæic Acid, $C_{16}H_{30}O_2$ (Gaïdic Acid, $C_{16}H_{30}O_2$)

The glyceride of this acid has been stated to occur in arachis oil by *Gössmann* and *Scheven*, and by *Schröder*. *Schoen*, however, could not detect any hypogæic acid in this oil, and although his statement is confirmed by *Bodenstein*,[3] yet the hypogæic acid prepared by the latter synthetically from stearolic acid has the properties of the acid obtained by *Schröder* from arachis oil. The acid is also stated to occur in maize oil.

Hypogæic acid crystallises in needles, melting at 33°-34° C., boiling at 236° C. under a pressure of 15 mm., and at 230° C. under a pressure of 10 mm.

On passing nitrous acid fumes through hypogæic acid, its stereometrical isomeride, **gaïdic acid**, melting at 39° C., is obtained.

Physetoleic Acid, $C_{16}H_{30}O_2$

This acid is said to occur as an ester in sperm oil; as a glyceride it has been found in Caspian seal oil.[4] It differs from hypogæic acid, in that it is not transformed into a stereometrical isomeride by nitrous

[1] *Liebig's Annalen*, 283, 65. Cp. also Rupe, Ronus, and Lotz, *Berichte*, 1902, 4265.

[2] Raymann, *Monatshefte für Chemie*, 6, 895. According to Ljubarsky the acid from the fat of Coccus axin (Mexico) has the composition $C_{16}H_{30}O_2$ (physetoleic ?)

[3] *Berichte*, 1894, 3397.

[4] Ljubarsky, *Journ. prakt. Chemie*, 1898, 26.

acid. Nor does it yield sebacic acid on distillation. The melting point of physetoleic acid is stated to be 30° C.

Lycopodic Acid, $C_{16}H_{30}O_2$

The glyceride of this fourth acid, having the composition $C_{16}H_{30}O_2$, has been discovered in the spores of lycopodium.[1] It differs from the above described isomerides by being liquid at the ordinary temperature. Potassium permanganate transforms it into dihydroxypalmitic acid; melting caustic potash splits it up into isobutyric and lauric acids.

Oleic Acid

$$C_{18}H_{34}O_2 = CH_3 . (CH_2)_{13} . C . H \\ \parallel \\ H . C . CH_2 . COOH ;^{2}$$

or

$$CH_3 . (CH_2)_7 . CH \\ \parallel \\ CH . (CH_2)_7 . COOH.^{3}$$

Oleic Acid is found in most vegetable and animal fats, especially in the liquid ones, in combination with glycerol. Large quantities of oleic acid are prepared commercially as a by-product in the manufacture of candles (*see chap. xv.*).

The chemically pure product can only be obtained with difficulty. A number of preparations sold commercially as "pure" oleic acid are obtained from almond oil, by separating the ether-soluble lead salts from those of the solid acids, but it should be noted that oleic acid so prepared still contains small quantities of less saturated acids (linolic, and perhaps linolenic). On the other hand, the oleic acid obtained on a large scale from tallow retains a few per cent of solid acids. I lay stress on these points, as a number of observations on oleic acid (so-called *acid. oleic. puriss*) have been made with an impure acid, and hence statements as to the solubility of the salts prepared with such acid must be accepted with reserve. Oleic acid can only be considered as chemically pure if its iodine value is 90, the theoretical value being 90·07. Most so-called pure oleic acids obtained in commerce widely deviate from this number, according as they contain solid acids or less saturated acids; even the best preparations have either iodine values varying from 82 to 84 on the one hand, or from 100 to 110 on the other.

The pure acid is best prepared from tallow (which contains practically no less saturated acids than oleic acid), by saponifying with caustic potash, precipitating the soap solution with lead acetate, and

[1] *Journ. Chem. Soc.* 1889, Abstracts, 741; 1059.
[2] Saytzeff, *Berichte*, 1894 (27), Ref. 577.
[3] Baruch, *Berichte*, 1894 (27), 173. Cp. also Lewkowitsch, *Journ. Soc. Chem. Ind.* 1897, 391.

extracting the dried lead salt with ether. The dissolved lead salt is decomposed with hydrochloric acid under ether, the liberated acid dissolved in ammonia and precipitated by means of barium chloride. Next, the barium salt is dried, boiled out with hot alcohol, and the hot solution allowed to crystallise. The crystallised salt is decomposed either by strong mineral acid or tartaric acid, as proposed by *Gottlieb*.[1] Exclusion of atmospheric air, although desirable, is not an essential point, for the older statements (which are still being copied from one text book into another), that oleic acid absorbs oxygen from the air, are erroneous. These statements are due to the fact that the older observers termed the fatty acids from linseed oil or semi-drying oils, oleic acid.

Oleic acid prepared in this manner will still contain traces of solid acids. As a method for removing the last traces of the latter I would suggest the conversion of the oleic acid into the chloro-iodo product, and separate the latter from the saturated acids by dissolving in an organic solvent and allowing to crystallise. From the crystallised chloro-iodo-oleic acid, oleic acid could then be obtained by heating with aniline or quinoline. *Farnsteiner* claims to have obtained pure oleic acid from olive oil by converting the mixed liquid olive oil acids into barium salts, and recrystallising the latter repeatedly from benzene containing a little alcohol (cp. p. 366). The pure acid is a colourless liquid free from smell, solidifying at 4° C. and melting at 14° C. It crystallises in the shape of needles. *Chevreul* gave the specific gravity at 14° C. as 0·898. More recent observations have led to the following numbers:—0·8908 at $\frac{11·8°}{4°}$ C., 0·898 at 15° C., 0·895 at 20° C., 0·889 at 30° C., 0·875 at 50° C., and 0·854 at $\frac{78·4°}{4°}$ C. The following table contains the numbers obtained by *Procter*[2] for a specimen of fairly pure oleic acid:—

Temperature, °C.	Specific Gravity.	Refractive Index.	Refractive Constants. $\frac{n-1}{d}$	Refractive Constants. $\frac{n^2-1}{(n^2+2)d}$
15	0·898	1·4638	0·5165	0·3072
20	0·895	1·4620	0·5159	0·3070
25	0·893	1·4603	0·5154	0·3069
30	0·889	1·4585	0·5158	0·3072
35	0·885	1·4566	0·5160	0·3075
40	0·882	1·4546	0·5154	0·3074
45	0·880	1·4528	0·5145	0·3071
50	0·875	1·4509	0·5153	0·3077
60	0·870	1·4471	0·5140	0·3072

Under ordinary pressure oleic acid cannot be distilled without undergoing decomposition; it is partially broken up into water, carbonic, acetic, caprylic, and capric acids; at the same time sebacic acid and hydrocarbons are formed. In a current of superheated steam

[1] *Liebig's Annalen*, 57 (1846), 38. [2] *Journ. Soc. Chem. Ind.* 1898, 1022.

it passes over, however, unchanged at a temperature of about 250° C. The following boiling points have been found by *Krafft* and *Nördlinger*,[1] and *Krafft* and *Weilandt*,[2] for the pressures given in the table :—

Boiling Point. °C.	Pressure mm. Mercury.
153·0	0
223·0	10
232·5	15
249·5	30
264·0	50
285·5-286·0	100

Oleic acid is insoluble in water, but dissolves readily in cold alcohol, even if the alcohol is diluted. On adding large quantities of water to the alcoholic solution the acid is thrown out. On this greater solubility of oleic acid in mixtures of water, alcohol, and acetic acid, compared with that of the solid fatty acids (palmitic and stearic), *David*[3] based a method of separating the several acids.

Oleic acid is converted into elaïdic acid when acted upon with nitrous acid at the ordinary temperature[4] (see p. 100). The same change takes place when it is treated with sodium bisulphite under pressure at 175°-180° C., or with sulphurous acid under pressure at 200° C. The reaction is, however, not a complete one, the change being a reversible one.[5]

On exposure to the light and air, oleic acid turns yellowish or yellow, acquires a rancid smell, and reddens blue litmus paper. *Scala*[6] isolated from oleic acid thus exposed the following products: œnanthaldehyde, formic, acetic, butyric, and œnanthic acids; also azelaïc and suberic acids (and dihydroxystearic acid ?). (The same substances were obtained from a very rancid olive oil.)

A sample of oleic acid which had been kept for some nineteen years is stated by *Senkowski*[7] to have deposited crystals of a melting point 48° C., whereas the unchanged oleic acid, as ascertained by the iodine value, formed only 32·1 per cent of the whole mass. In the deposited crystals an ester occurred which was calculated to 8·3 per cent of stearolactone; it is doubtful whether the remainder consisted of hydroxystearic acid. What change did occur in this oleic acid has not been further explained. From my own experience I can state that a sample of commercial oleic acid from tallow, kept eight years in an iron drum, which was very frequently opened, had still retained the same neutralisation value, and practically the same iodine value it had originally, viz., 84.

[1] *Journ. Chem. Soc.* 1889, Abstracts, 691. [2] *Berichte*, 1896, 1324.

[3] *Journ. Chem. Soc.* 34, 1011.

[4] Lidoff states (*Analyst*, 1895, 178), that by the action of nitrous oxides on oleic acid at 80°-85° C. an increase of weight takes place, and the iodine value of the product falls to 9 per cent. Experiments made by the writer show, however, that elaïdic acid is formed and the apparent low iodine value is due to the action of nitrous acid, left in the fatty acid, on potassium iodide (*Journ. Soc. Chem. Ind.* 1897, 390).

[5] Cp. Albitzky, *Journ. f. prakt. Chemie*, 1903.

[6] *Staz. Sper. Agr. Ital.* 30, 613. [7] *Zeit. f. physiolog. Chem.* 1898, 434.

On blowing air through oleic acid at 120° C., for 2, 4, 6, and 10 hours, I obtained[1] 0·62, 2·6, 3·5, and 6·0 per cent of "oxidised" acids (insoluble in petroleum ether) respectively; the specific gravities had risen in the same order from 0·8980 to 0·9098, 0·9121, 0·9123, and 0·9238 respectively. Similarly on digesting oleic acid with sulphur at a temperature between 130° and 150° C. the sulphur is absorbed, without evolution of sulphuretted hydrogen, an addition product being apparently formed (see chap. xv.). At higher temperatures, from 200° to 300° C., sulphuretted hydrogen is evolved.

Oleic acid absorbs one molecule of bromine forming dibromostearic acid;[2] similarly iodochloride is absorbed to form a saturated acid. On reducing these products with zinc and hydrochloric acid, oleic acid is regenerated. When heated with melted caustic potash, oleic acid is broken down to palmitic acid (see p. 92), oxalic and acetic acids being obtained as secondary products.

Oleic acid dissolves in cold concentrated sulphuric acid to form stearic acid hydrogen sulphate, $C_{18}H_{35}(SO_4H)O_2$; on boiling this product with water, sulphuric acid is split off, and β-hydroxystearic acid is formed conjointly with a small quantity of stearolactone (*Geitel*); (see "Turkey-red Oil," chap. xv.).[3] A similar change takes place on heating oleic acid with zinc chloride to 185° C. (see "Commercial Stearic Acid," chap. xv.). According to *Saytzeff*,[4] by the interaction of sulphuric acid with oleic acid, hydroxystearosulphuric acid $C_{17}H_{34}\begin{cases}OSO_2OH\\COOH\end{cases}$ is formed. On boiling with water, hydroxystearic acid is obtained, together with a mixture of anhydrides of the latter acid, which is sparingly soluble in 80 per cent alcohol. These anhydrides may be roughly differentiated by the facility with which they are converted into salts of hydroxystearic acid on heating with alkalis.

Sulphuric acid of 85 per cent acts on oleic acid like concentrated acid.[5]

The reduction of oleic acid to stearic acid by means of hydriodic acid and phosphorus has been considered already. *P. de Wilde* and *Reychler*[6] tried to convert oleic acid into the more valuable stearic acid by heating the former, mixed with 1 per cent of iodine, in autoclaves up to 270°-280° C. A mixture of fatty substances resulted, melting from 50°-55° C., which they separated by distillation in a current of superheated steam into a residue insoluble in alcohol, a distillate containing stearic acid, and a liquid, which cannot be converted into

[1] Lewkowitsch, *Analyst*, 1899, 322.

[2] The barium salt of the dibromostearic acid is wax-like, sparingly soluble in alcohol and ether at the ordinary temperature, but readily soluble in a mixture of alcohol and benzene (Farnsteiner, *Zeit. Unters. Nahrungs. u. Genussm.* 1899, 15). The lead salt is viscous, sparingly soluble in cold 95 per cent alcohol, but dissolves readily in ether, petroleum ether, ether-alcohol, benzene, and a mixture of benzene and alcohol.

[3] Cp. also *Journ. Soc. Chem. Ind.* 1897, 390.

[4] *Journ. f. prakt. Chem.* 35, 369, 57 (1898), 26.

[5] Twitchell, *Journ. Soc. Chem. Ind.* 1897, 1002.

[6] *Journ. Soc. Chem. Ind.* 1889, 466.

stearic acid by repeating the process. The yield of stearic acid only reaches 70 per cent, and but one-third of the iodine can be recovered. Thus the costliness of the process prevents its introduction into candle-works. On oxidising oleic acid with nitric acid, the dibasic acids adipic, pimelic, and suberic acids are obtained;[1] at the same time all the volatile acids, from formic acid up to, and including capric acid are formed. Potassium permanganate in acid solution also yields dibasic acids in considerable quantities. On oxidising oleic acid with an excess of potassium permanganate in dilute alkaline solution in the cold, dihydroxystearic acid is chiefly formed. *Edmed*[2] states that he obtained 60 per cent of dihydroxystearic acid, a small quantity of pelargonic acid, 16 per cent of azelaïc acid, and 16 per cent of oxalic acid when oxidising oleic acid at 60° C. If the oxidation with potassium permanganate be carried out in presence of only so much caustic potash as is required to neutralise the oleic acid, besides dihydroxystearic acid, ketohydroxystearic acid is obtained.[3] On oxidising oleic acid with persulphuric acid dihydroxystearidic acid is formed.[4]

The salts of the alkali-metals—oleic acid soaps—are thrown out from their aqueous solution by adding strong caustic alkali, common salt, or other soluble mineral salts. Their behaviour to water has been described above (p. 80). All the oleates are considerably softer than the corresponding salts of palmitic and stearic acids; most of them melt without decomposition.

Sodium oleate, $NaC_{18}H_{33}O_2$, is prepared by crystallisation from absolute alcohol (not from dilute alcohol). It dissolves in 10 parts of water at 12° C., or in 20·6 parts of alcohol, specific gravity 0·821, at 13° C., or in 100 parts of boiling ether. The dry salt melts at 232°-235° C.

Potassium oleate, $KC_{18}H_{33}O_2$, forms a transparent, jelly-like mass, far more readily soluble in water, alcohol, and ether than the sodium salt, 1 part of the salt requiring 4 parts of water, or 2·15 parts of alcohol, or 29·1 parts of boiling ether.

Lithium oleate, $LiC_{18}H_{33}O_2$, is soluble in hot alcohol, insoluble in ether, carbon bisulphide, and benzene. (See Appendix.)

The metallic oleates behave with water in much the same way as the metallic salts of palmitic and stearic acids; they are mostly soluble in alcohol; some are also dissolved by ether.

Calcium oleate, $Ca(C_{18}H_{33}O_2)_2$, forms a powder insoluble in alcohol and ether. It is somewhat soluble in concentrated sugar solution. Thus 200 c.c. of a 10 per cent sugar solution dissolve after digesting for 1 hour at 19·5° C., 35° C., 50° C., and 65° C., 0·0661, 0·1767, 0·450, and 0·726 grm. respectively.[5]

Barium oleate, $Ba(C_{18}H_{33}O_2)_2$, is a crystalline powder insoluble in water, and but sparingly soluble in boiling alcohol. At the temperature of 100° C. it conglutinates without, however, becoming liquid.

[1] Lewkowitsch, *Journ. f. prakt. Chem.* 1879. [2] *Journ. Chem. Soc.* 73, 627.
[3] Holde and Marcusson, *Berichte*, 1903, 2657. [4] Albitzky, *Berichte*, 1900, 2909.
[5] *Zeit. f. angew. Chem.* 1901, 1115.

Dried barium oleate[1] is very sparingly soluble in hot benzene; in a mixture of hot benzene and absolute alcohol it dissolves with great difficulty on boiling. In the presence of small amounts of water, however, barium oleate easily dissolves in hot benzene; thus it is sufficient to admix with the benzene 5 per cent, or even less, of 95 per cent alcohol to effect solution. From the hot benzene solution the salt separates out on cooling almost completely (in the form of a crystalline powder consisting of long and very thin needles or laminæ of silvery lustre); 100 c.c. of the filtrate contained at 11° C. only 0·015 grm., and at 17·5° C. 0·023 grm. barium oleate. Chloroform and petroleum ether show a similar behaviour.

Aluminium oleate, $Al(C_{18}H_{33}O_2)_3$, forms a jelly-like mass, insoluble in alcohol, and sparingly soluble in hot ether and petroleum ether. In the arts it is used as an "oil-thickener."

Silver oleate, $AgC_{18}H_{33}O_2$, is nearly insoluble in ether. (Difference from silver salt of rosin acids.)

Copper oleate, $Cu(C_{18}H_{33}O_2)_2$, melts at 100° C. to a green oil. It dissolves readily in cold ether to a green solution, in alcohol to a bluish-green solution.

Lead oleate, $Pb(C_{18}H_{33}O_2)_2$, is a white powder, melting at 80° C. to a yellow oil. It is soluble in ether, and may thus be separated from the saturated acids (palmitic, stearic, etc., and also from elaïdic and isooleic acids). This separation, however, is not a complete one.[2] Lead oleate is also soluble in petroleum ether, but only slightly soluble in absolute alcohol (*Twitchell*).

The methyl-, and ethyl-esters are liquids of the specific gravity 0·879 at 18° C., and 0·871 at 16° C. respectively. (See Appendix.)

In near relation to oleic acid stand its isomerides, *elaïdic acid* and *isooleic acid*.

Elaïdic acid is obtained by allowing nitrous acid fumes, or a nitrite and nitric acid, to act on oleic acid at the ordinary temperature; after a short time the oleic acid is changed into its stereometrical isomeride, elaïdic acid. The separation of elaïdic acid from the unchanged oleic acid is readily effected by crystallisation from ether, or by separating the lead salts by means of ether or benzene. The constitution of elaïdic acid may be represented by one of the following graphic formulæ :—

$$\begin{array}{c} CH_3 \cdot (CH_2)_{13} \cdot CH \\ \| \\ COOH \cdot CH_2 \cdot CH \end{array} \quad \text{or} \quad \begin{array}{c} CH_3 \cdot (CH_2)_7 \cdot CH \\ \| \\ COOH \cdot (CH_2)_7 \cdot CH \end{array}$$

The acid crystallises from alcohol in plates melting at 44·5° C. This melting point has been ascertained by me from a repeatedly recrystallised elaïdic acid prepared in my laboratory. I found the same melting point for a specimen carefully prepared by *Geitel*.[3]

[1] Farnsteiner, *Zeit. f. Untersuchung d. Nahrg. u. Genussmittel*, 1901, 63.
[2] Lewkowitsch, *Journ. Soc. Chem. Ind.* 1890, 845; cp. also chap. viii.
[3] *Analyst*, 1899, 258.

Farnsteiner[1] gives 43·5°-44·5° C. as the melting point. Hence, *Saytzeff's*[2] statement that elaïdic acid melts at 51°-52° C. (and solidifies at 44°-45° C.) must be accepted with reserve. The specific gravity is 0·8505 at $\frac{79·4°}{4°}$ C.

Elaïdic acid distils almost unchanged. The following boiling points have been ascertained by *Krafft* and *Nördlinger*:—

Boiling Point. °C.	Pressure. mm. Mercury.
154	0
225	10
234	15
251·5	30
266	50
287·8-288·0	100

The barium, lead, and silver salts of elaïdic acid are very sparingly soluble in alcohol and ether. Lead elaïdate simulates, as regards solubility, the lead salts of the solid saturated fatty acids (cp. p. 80). The following table gives some data:—

100 c.c. of	Dissolve of Lead Salt.	At °C.
Ether	0·0046 to 0·0086 grms.	16-20
Benzene	*0·0040*	*16-20*
" after dissolving the salt in the hot and allowing to crystallise.		
After 1 hour	0·0148	16
After 17 hours	0·0028	16
Absolute alcohol—after dissolving the salt in the hot and allowing to crystallise—after 18 hours	0·0100	17

Elaïdic acid can be converted in its turn into ordinary oleic acid by boiling iodostearic acid, prepared from elaïdic acid, with alcoholic potash; simultaneously some isooleic acid is formed.[3]

On heating elaïdic acid with sulphurous acid under pressure, about 20 per cent is converted into ordinary oleic acid.[4] On oxidising elaïdic acid by means of potassium permanganate in alkaline solution in the cold, dihydroxystearidic acid is obtained,[5] whilst pelargonic, azelaic, and oxalic acids are formed as secondary products. *Edmed*[6] ascertained the following percentages of oxidation products: dihydroxystearidic acid, of the melting point 99° C., 33 per cent; pelargonic acid, 13 to 14 per cent; azelaic acid, 26 per cent; oxalic acid 15-20 per cent (cp. above, p. 106). Heated with melted caustic potash elaïdic acid yields, like ordinary oleic acid, palmitic acid. By the action of concentrated sulphuric acid on

[1] *Zeit. f. Unters. d. Nahrungs. u. Genussm.* 1899, 5.
[2] *Journ. prakt. Chemie*, 50 (1894), 175.
[3] Lebedeff, *Journ. f. prakt. Chemie*, 50 (1894), 61.
[4] Albitzky, *Journ. prakt. Chemie*, 61 (1900), 65.
[5] *Berichte*, 1894, 173. [6] *Journ. Chem. Soc.* 1898, 631.

elaïdic acid, anhydrides are chiefly produced, which yield on treatment with alcoholic potash β-hydroxystearic acid.[1]

The methyl-, and ethyl-esters are liquids of the specific gravity 0·872 at 18° C., and 0·868 at 18° C. respectively.

Isooleic (Para-oleic), Solid Oleic Acid, $CH_3 . (CH_2)_{14} . C . H$
$$\begin{array}{c} \| \\ H . C . CO_2H \end{array}$$
is prepared, according to *Saytzeff*,[2] from β-hydroxystearic acid by distilling it under diminished pressure, when a distillate is obtained consisting of a mixture of ordinary oleic and isooleic acids, together with some unchanged hydroxystearic acid. The pure isooleic acid is obtained by allowing the mixture to crystallise from its ethereal solution and converting the crystallised acids into their zinc salts; these are exhausted with boiling alcohol, when zinc hydroxystearate remains undissolved, whilst from the alcoholic solution of zinc isooleate and zinc oleate the former separates out on cooling. Isooleic acid is then separated from its zinc salt by sulphuric acid and purified by repeated crystallisation from ether. The mixture of the two isomeric acids can be more readily resolved into its components by crystallising from petroleum ether.[3]

Isooleic acid is also formed, when iodostearic acid, obtained by the action of hydriodic acid on ordinary oleic acid or elaïdic acid, is heated with alcoholic potash in a flask connected with an inverted condenser. The resulting product contains isooleic acid, together with unchanged oleic acid.

Considerable quantities of isooleic acid occur in commercial stearic acid, obtained by "acid saponification" and subsequent distillation (cp. chap. xv.).

Isooleic acid forms transparent, rhombic plates (from ether), melting from 44° to 45° C. It is very easily soluble in alcohol, considerably less so in ether. It absorbs, like ordinary oleic acid, two atoms of bromine or iodine and undergoes the same change as oleic acid when treated with melted caustic potash. With potassium permanganate, a dihydroxystearic acid is obtained which differs from that obtained from ordinary oleic acid (cp. p. 124). On treating isooleic acid with concentrated sulphuric acid, and subsequently boiling the product with water, two isomeric hydroxystearic acids are formed (see p. 122), differing in their behaviour when subjected to distillation *in vacuo*.

The *calcium* salt $Ca(C_{18}H_{33}O_2)_2 + H_2O$, is insoluble in hot alcohol.

The *lead* salt of isooleic acid is considerably less soluble in ether than lead oleate.

Rapic Acid, $C_{18}H_{34}O_2$

The glyceride of rapic acid occurs, according to *Reimer* and *Will*,[4] in rape oil. Rapic acid does not solidify on cooling, and does not

[1] Tscherbakoff and Saytzeff, *Journ. f. prakt. Chemie*, 57 (1898), 27.
[2] M. and A. Saytzeff, *Journ. f. prakt. Chemie*, 1888, 442.
[3] Shukoff and Schestakoff, *Journ. f. prakt. Chemie*, 1903 (67), 416.
[4] *Journ. Soc. Chem. Ind.* 1887, 732.

yield a solid isomeride when acted upon by nitrous acid. The sodium salt forms a gelatinous mass easily soluble in water; the zinc salt is crystalline, dissolves easily in alcohol and ether, and melts at 78° C.

Reimer and *Will* assigned to the acid the formula $C_{18}H_{34}O_3$, but rapic acid cannot be an hydroxylated acid, as the acetyl value of rape oil is very low (cp. chap. xiv.). Recently *Zellner*[1] has shown that rapic acid has the composition $C_{18}H_{34}O_2$, as he was able to convert it into an iodo-compound yielding stearic acid on reduction with zinc and hydrochloric acid. The analysis of zinc rapate confirms the formula $C_{18}H_{34}O_2$.

Doeglic Acid, $C_{19}H_{36}O_2$

The existence of this acid is somewhat doubtful, and it may possibly be identical with oleic acid. It has been stated by *Scharling*[2] to occur in Arctic sperm oil as a dodecatyl ester.

Jecoleic Acid, $C_{19}H_{36}O_2$

An acid of this composition is assumed by *Heyerdahl* to occur in cod liver oil,[3] inasmuch as he obtained a dihydroxyjecoleic acid (cp. p. 124) by oxidising the cod liver oil fatty acids with potassium permanganate. Jecoleic acid is stated to form at least 20 per cent of the liquid fatty acids in cod liver oil.

Erucic Acid

$$C_{22}H_{42}O_2 = \begin{array}{l} C_8H_{17} - CH \\ \qquad\quad \| \\ \qquad H - C.(CH_2)_{11}.COOH \end{array};$$[4]

or

$$\begin{array}{l} CH_3 - (CH_2)_{17} - CH \\ \qquad\qquad\qquad \| \\ \qquad\qquad\quad CH.CH_2.COOH \end{array}$$[5]

The glyceride of this acid occurs in rape oil, in black and white mustard oils,[6] and in fish oils (?);[7] the solid glyceride in Tropæolum oil is almost pure trierucin. The acid crystallises from alcohol in long, fine needles melting from 33° to 34° C. The following boiling points have been found by *Krafft* and *Nördlinger*:—

Boiling Point. °C.	Pressure. mm. Mercury.
179	0
254·5	10
264	15
281	30

[1] *Journ. Soc. Chem. Ind.* 1896, 661.
[2] *Journ. prakt. Chemie*, 43 (1848), 257.
[3] *Cod Liver Oil and Chemistry*, p. xcviii.
[4] Liebermann, *Berichte*, 1893, 1869.
[5] Alexandroff and Saytzeff, *Journ. f. prakt. Chemie*, 49 (1894), 63.
[6] The occurrence of erucic acid in grape seed oil (Fitz, *Berichte*, 1871, 444) is doubtful (cp. Grape Seed Oil).
[7] Bull. *Journ. Soc. Chem. Ind.* 1900, 73; *Chem. Zeit.* 1899, 996.

Erucic acid much resembles oleic acid in its properties. Thus it absorbs two atoms of bromine or iodine; nitrous acid and sulphurous acid under pressure at high temperatures (cp. "Oleic Acid," p. 104), as also bisulphites, convert it into its stereometrical isomeride *brassidic acid*, $C_{22}H_{42}O_2$; heated with hydriodic acid and phosphorus it is reduced to behenic acid; melting caustic potash splits it up into acetic and arachidic acids; on oxidation with potassium permanganate it yields dihydroxybehenic acid. On oxidation with nitric acid, nonylic and brassylic acids are obtained. The *sodium* salt melts at 230°-235° C. The *lead* salt of erucic acid is but sparingly soluble in ether, differing in this respect from oleic acid.

The ethyl ester is a liquid boiling above 360° C. without decomposition.

Brassidic acid,

$$\begin{matrix} C_8H_{17}\,.\,CH \\ \| \\ COOH\,.\,(CH_2)_{11}\,.\,CH, \end{matrix} \quad \text{or} \quad \begin{matrix} CH_3\,.\,(CH_2)_{17} - CH \\ \| \\ COOH\,.\,CH_2 - CH \end{matrix}$$

crystallises from alcohol in laminæ, having the melting point 65° C., and solidifying point 56° C.; it boils *in vacuo* at 180° C., and under a pressure of 15 mm. at 265° C.

The sodium salt melts at 245°-248° C. The lead salt is very sparingly soluble in hot ether. The ethyl ester crystallises from alcohol in shining laminæ, melting at 29°-30° C. The ester boils above 360° without undergoing decomposition.

Isoerucic acid, $CH_3\,.\,(CH_2)_{17}\,.\,CH_2\,.\,CH = CH\,.\,CO_2H$,[1] is obtained from iodo-behenic acid by boiling with alcoholic potash. The iodo-behenic acid may be prepared from either erucic or behenic acid[2] (cp. "Isooleic Acid," p. 109).

Isoerucic acid crystallises from alcohol in plates, melting at 54°-56° C., solidifying at 52°-51° C.

III.—Acids of the Linolic Series, $C_nH_{2n-4}O_2$

The acids belonging to this series are characterised by their capability of absorbing four atoms of bromine or iodine, and by the solubility of their lead and barium salts in ether. They are not converted into solid isomerides by nitrous acid. They readily absorb oxygen on exposure to the air; this important property is made use of in the arts (drying oils).

Isomeric with the acids described below are the solid palmitolic, stearolic, and behenolic acids. These latter acids have hitherto not been found to occur naturally; hence they will not be described here.

[1] Saytzeff, *Journ. f. prakt. Chemie*, 1892 (45), 301.
[2] Alexandroff and Saytzeff, *ibid.* 1894, 49, 58. Saytzeff, *ibid.* 1894 (50), 65.

LINOLIC ACID, $C_{18}H_{32}O_2$

The glyceride of linolic acid occurs in considerable proportions in drying and semi-drying oils, and is most readily obtained from maize and cotton seed oils. Recent researches have shown that a large number of non-drying oils (almond, arachis, olive), and even solid fats (hare fat, horse fat, lard) contain linolic acid in notable quantities.

Reformatzky,[1] claims to have prepared the pure acid by hydrolysing pure ethyl linolate; but according to *Hazura's* researches it is very likely that *Reformatzky's* linolic acid is a mixture of the unsaturated acids occurring in linseed oil, and containing acids of the formula $C_{18}H_{30}O_2$ (cp. "Linseed Oil," chap. xiv.).

Linolic acid is a yellowish oil, which remains fluid even at a temperature of $-18°$ C.; its specific gravity is 0·9206 at 14° C. It has a slight acid reaction, and dissolves readily in alcohol and ether. Nitrous acid does not produce a solid acid from linolic acid (important difference from acids of the oleic series). Linolic acid absorbs oxygen rapidly from the atmosphere, and when exposed in thin films to the air it is converted within a few days into a solid resinous substance; and after a more prolonged exposure it forms a neutral body insoluble in ether. The latter compound is the so-called "linoxyn." [2]

In concentrated sulphuric acid, linolic acid dissolves readily; the sulpho-compound is insoluble in petroleum ether.[3]

Linolic acid absorbs four atoms of bromine, forming the **tetrabromide** $C_{18}H_{32}O_2Br_4$, melting point 114°-115° C. (*Hazura*); 114° C. (*Lewkowitsch*); 113°-114° C. (*Farnsteiner*). Excess of bromine does not produce the hexabromostearic acid obtainable from linolenic acid (p. 114); a small quantity is, however, converted into another bromide (soluble in petroleum ether at the ordinary temperature). At higher temperatures about 22 per cent are so converted. The tetrabromide is easily soluble in ether, alcohol, benzene, chloroform, and glacial acetic acid, but sparingly soluble in petroleum ether (important difference from oleic acid, cp. chap. viii.). The tetrabromide is reduced to linolic acid by means of zinc and alcoholic hydrochloric acid.

On oxidising linolic acid with a dilute solution of potassium permanganate in the cold, tetrahydroxystearic or sativic acid $C_{18}H_{36}O_6$ (cp. p. 126) is formed. By heating linolic acid with phosphorus and hydriodic acid to 200° C. stearic acid is obtained.

The metallic salts of linolic acid are amorphous, with the exception of the zinc salt. Barium and calcium linolates are soluble in boiling alcohol; the calcium, barium, zinc, copper, and lead salts dissolve in ether. Barium linolate is easily soluble in benzene and petroleum ether (important difference from barium oleate). The lead salt of the tetrabromide is very sparingly soluble in cold ether

[1] *Journ. Soc. Chem. Ind.* 1890, 744. [2] *Ibid.* 1888, 680.
[3] Twitchell, *Journ. Soc. Chem. Ind.* 1897, 1004.

and benzene; in a mixture of two parts of benzene and one part of alcohol the salt dissolves easily in the hot, separating out in crystals on cooling. Linolates absorb oxygen more readily than the free acid ("Driers," chap. xv.).

Tariric Acid, $C_{18}H_{32}O_2$

This isomeride of linolic acid has been found[1] combined with glycerol in the fat from the seeds of a Guatemalan *Picramnia* (Tariri), and also in the fat from *Picramnia Camboita*.[2]

Tariric acid melts at 50·5° C. It absorbs four atoms of bromine forming a tetrabromide, melting point 125° C. The potassium salt is only slightly soluble in 98 per cent alcohol, 100 parts of the latter dissolving 2·48 parts of tariric acid at 15° C.

On reducing tariric acid with hydriodic acid and amorphous phosphorus, stearic acid[3] is obtained. On oxidising the acid with potassium permanganate in alkaline solution, as also with fuming nitric acid, adipic and lauric acids are obtained. Hence *Arnaud*[4] ascribes to tariric acid the constitutional formula $CH_3 . (CH_2)_{10} . C : C . (CH_2)_4 . CO_2H$.

Millet Oil Acid, $C_{18}H_{32}O_2$

The existence of this acid, assumed by *Kassner*[5] to occur as a glyceride in millet oil, is somewhat doubtful.

Telfairic Acid, $C_{18}H_{32}O_2$

This acid occurs as a glyceride in koëme oil;[6] it has been isolated from the mixed fatty acids of koëme oil by fractional distillation of the liquid fatty acids.

The acid solidifies at 6° C. and boils at 220°-225° C. under a pressure of 13 mm. Its tetrabromide melts at 57°-58° C. By oxidation with potassium permanganate in dilute alkaline solution at 0° C. a tetrahydroxystearic acid of the melting point 177° C. is obtained.

Elæomargaric Acid, $C_{18}H_{32}O_2$

The glyceride of this acid occurs in tung oil (Chinese, or Japanese wood oil). The free acid crystallises in rhombic plates having the melting point 48° C. (*Cloëz*, *Maquenne*), 43·8° C. (*de Negri* and *Sburlati*), 43°-44° C. (*Kametaka*). The acid readily absorbs oxygen from the atmosphere, and becomes resinous. Protected from light, the alcoholic (or ethereal) solution of the acid remains unchanged. On exposure to light, however, crystals are deposited from the alcoholic solution melting at 71° C., having the same composition as elæo-

[1] *Journ. Soc. Chem. Ind.* 1892, 619.
[2] Grützner, *Chem. Zeit.* 1893, 1851.
[3] Arnaud, *Compt. rend.* 122, 1000.
[4] *Ibid.* 134, 437.
[5] *Journ. Chem. Soc.* 1888, Abstr. 673.
[6] Thoms, *Arch. d. Pharm.* 238 (1900), 48.

margaric acid. According to *Maquenne*[1] this latter acid, termed by *Cloëz* elæostearic acid, is a stereometric isomeride of elæomargaric acid, and stands to it in the same relationship as does elaïdic acid to oleic acid. *Maquenne* found that the elæomargaric acid to which *Cloëz* had ascribed the formula $C_{17}H_{30}O_2$, contained 18 carbon atoms. He assigned to the characteristic tung oil acid the formula $C_{18}H_{30}O_2$, and accordingly proposed to change the name elæomargaric acid into α-elæostearic acid, assigning to the isomeride melting at 71° C. the name β-elæostearic acid.

The name elæostearic acid has not been adopted here since it was found in my laboratory,[2] that the formula $C_{18}H_{30}O_2$ cannot be correct, inasmuch as no hexabromide could be obtained from tung oil. Since then *Kametaka*[3] has shown that the true composition of the acid is $C_{18}H_{32}O_2$.

The acid must be considered a stereoisomeride of linolic acid, for it yields on bromination a tetrabromide, which is identical with the tetrabromide obtained from linolic acid; on oxidation elæomargaric acid yields sativic acid.

IV.—Acids of the Linolenic Series, $C_nH_{2n-6}O_2$

The acids of the linolenic series assimilate six atoms of bromine or iodine, and absorb oxygen readily. Their lead salts are easily soluble in ether. Nitrous acid does not produce solid isomerides.

Linolenic Acid, $C_{18}H_{30}O_2$

The glyceride of this acid occurs in large quantities in the drying oils, especially in linseed oil. The free acid has been prepared by *Hazura*,[4] and later on by *Hehner* and *Mitchell*,[5] from a hexabromide, obtained on brominating the mixed liquid acids of linseed oil. This hexabromide melts at 177° C. (*Hazura*), 180°-181° C. (*Hehner* and *Mitchell*). On reduction with zinc and alcoholic hydrochloric acid it yields linolenic acid. The acid obtained by *Hehner* and *Mitchell* is a nearly colourless oil, of the specific gravity 0·9228 at 15·5° C. (water at 15·5° C. = 1); it absorbs oxygen from the air very rapidly, thereby becoming dark brown. Potassium permanganate oxidises linolenic acid to hexahydroxystearic (linusic) acid (cp. p. 126). *Reformatzky*[6] considers *Hazura's* hexabromide to be a dibromo- (substitution product) derivative of the tetrabromide of linolic acid, and throws doubt on the existence of linusic acid, which he considers to be a product of oxidation of tetrahydroxystearic acid. In *Reformatzky's* opinion linolenic acid is identical with linolic acid. It must, however, be pointed out in support of *Hazura's* views, that his acid

[1] *Compt. rend.* 13, 135, 696.
[2] Walker and Warburton, *Analyst*, 1902, 237.
[3] *Journ. Chem. Soc.* 1903, 1042.
[4] *Journ. Soc. Chem. Ind.* 1888, 506.
[5] *Analyst*, 1898, 313.
[6] *Journ. Soc. Chem. Ind.* 1890, 744.

absorbs 245 per cent of iodine (*Hehner* and *Mitchell's* acid absorbed 241·8 per cent), theory requiring for an acid of the formula $C_{18}H_{30}O_2$ 274 per cent, whilst linolic acid is only able to assimilate 181 per cent.

The physical properties of linolenic acid resemble those of linolic acid with the exception of its odour, which is similar to that of fish oils.

Isolinolenic Acid, $C_{18}H_{30}O_2$

This acid has not yet been isolated, but its existence, as a glyceride in linseed oil, is inferred by *Hazura*[1] from the fact that he obtained isolinusic acid, an isomeride of linusic acid, on oxidising the mixed linseed oil acids with potassium permanganate.

Jecoric Acid, $C_{18}H_{30}O_2$

Fahrion[2] assumes the existence of this acid in sardine oil from the analyses of the barium, calcium, and magnesium salts. Other analytical data, however, as ultimate analysis, neutralisation number, iodine value, do not agree with those required by theory. The existence of this acid is therefore somewhat doubtful. Jecoric acid does not conform to *Hazura's* rule, inasmuch as it does not yield a hydroxylated acid on oxidation, only volatile acids and carbon dioxide being obtained.

V.—Acids of the Series $C_nH_{2n-8}O_2$

Isanic Acid, $C_{14}H_{20}O_2$

Isanic acid[3] has been isolated from the oil in the seeds of I'Sano or Ungueko (a large tree of the *Oleaceæ* family, growing in the French Congo); it is stated that its quantity in the oil amounts to about 10 per cent of the total mixed fatty acids.

The acid forms foliated crystals (from ether), melting at 41° C.; it is readily soluble in strong alcohol, ether, chloroform, benzene, acetone, methyl alcohol, and petroleum ether. It possesses a peculiar odour, which it imparts to the seeds, and is extremely susceptible to change of colour on exposure to air, turning thereby rose-red, the tinge deepening with the increased absorption of oxygen. Ether leaves the oxidised rose-coloured substance undissolved.

The formula given above seems doubtful, although derived from analyses of the acid and the silver and barium salts. The cryoscopic determination of the molecular weight gave 217 ($C_{14}H_{20}O_2 = 220$), but the acid absorbed about 2 molecules of bromine only. Endeavours to reduce the acid by means of hydriodic acid did not lead to conclusive results.

[1] *Journ. Soc. Chem. Ind.* 1888, 506. [2] *Ibid.* 1893, 938. [3] *Ibid.* 1896, 660.

Therapic Acid, $C_{17}H_{26}O_2$

The occurrence of an acid of this formula is inferred by *Heyerdahl*[1] from a bromine product $C_{17}H_{26}Br_8O_2$ which he obtained on brominating the cod liver oil fatty acids. Therapic acid is stated to occur in cod liver oil to the extent of 20 per cent; this name has been chosen by *Heyerdahl* to express his opinion that the acid plays the most important part in the therapeutical effect of cod liver oil.

Acids having the formulæ $C_{20}H_{32}O_2$ and $C_{24}H_{40}O_2$ are, on the strength of very high iodine values, assumed by *Bull*[2] to occur in herring oil.

VI.—Hydroxylated Acids, $C_nH_{2n}O_3$

Lanopalmic Acid, $C_{16}H_{32}O_3$

Lanopalmic acid has been isolated from that portion of the wool wax acids which forms potash soaps readily soluble in cold alcohol (chap. xiv.).

Lanopalmic acid crystallises from dilute alcohol in radiated crystals, melting at 87°-88° C., and solidifying at 85°-83° C. It is insoluble in water, but dissolves in it on boiling, in the presence of a small quantity of alcohol, and separates on cooling as a white crystalline magma. The usual organic solvents dissolve it readily.

Aqueous alkalis do not readily dissolve the acid; on adding, however, a little alcohol and heating, alkali salts are formed. The alkali salts exist in aqueous solution only in the hot; on cooling, they are dissociated into acid salts, which separate, and into free alkali.

The magnesium salt is insoluble in hot alcohol. The calcium salt dissolves easily in boiling absolute alcohol, but sparingly in 95 per cent alcohol.

An acid of the formula $C_{21}H_{42}O_3$ occurs, combined with alcohols, in carnaüba wax.[3] The free acid does not appear to exist in the free state, its inner anhydride, or lactone, being obtained, whenever the acid itself would be expected.

Cocceric Acid, $C_{31}H_{62}O_3$

Cocceric acid occurs in cochineal wax[4] combined with cocceryl alcohol. The acid forms a crystalline powder (from alcohol), melting point 92°-93° C., and dissolves sparingly in cold alcohol, ether, benzene, petroleum ether, and glacial acetic acid. On oxidising

[1] *Cod Liver Oil and Chemistry*, p. xcv.
[2] *Journ. Soc. Chem. Ind.* 1900, 73; *Chem. Zeit.* 1899, 996.
[3] *Journ. Soc. Chem. Ind.* 1884, 448. [4] *Ibid.* 1885. 585.

cocceric acid with chromic acid in acetic acid solution a pentadecylic acid is formed.[1]

VII.—Acids of the Ricinoleic Series. Hydroxylated Acids, $C_nH_{2n-2}O_3$

Ricinoleic Acid,

$$C_{18}H_{34}O_3{}^{2} = C_6H_{13} . CH(OH) . CH_2 . CH \\ \Vert \\ C . H . (CH_2)_7 . COOH$$

(Isomerides: Isoricinoleic Acid, $C_{18}H_{34}O_3$; Ricinelaïdic Acid, $C_{18}H_{34}O_3$; Ricinic Acid, $C_{18}H_{34}O_3$)

Ricinoleic Acid occurs, combined with glycerol, in large quantities in castor oil. The crude ricinoleic acid obtained by saponifying castor oil and decomposing the soap with a mineral acid represents at the ordinary temperature a thick oil of specific gravity 0·9509 at 15·5° C. On cooling to −6° to −10° C. the acid solidifies completely. *Krafft*[3] has obtained from the crude acid, by cooling to 0° and gradually pressing at temperatures not exceeding 12° C., a white, odourless, hard, crystalline mass melting at 16°-17° C., which he considered to be the pure acid. *Juillard*,[4] however, has shown that the acid so prepared still contains stearic and (natural) dihydroxystearic acids. The pure acid is best obtained from the barium salt after purifying the latter by repeated crystallisation from alcohol. The pure acid melts at 4°-5° C.; it is miscible in alcohol and ether in every proportion. The acid cannot be distilled without undergoing decomposition, even under a pressure of only 15 mm. Amongst the products of decomposition are found undecylenic and œnanthaldehyde, and, according to *Mangold*,[5] an acid of the formula $C_{18}H_{32}O_2$. The ricinoleic acid prepared from castor oil is optically active, as indicated in the above-given constitutional formula by the asymmetric carbon atom. *Walden*[6] found for the acid in acetone solution $[\alpha]_D = +6{\cdot}25$.

According to *H. Meyer*[7] ricinoleic acid becomes polymerised on standing, forming polyricinoleic acids; these are easily re-converted into ricinoleic acid on boiling with alcoholic potash. Thus, an acid of the specific gravity 0·9460 at 12° C. had become viscous after eight years' standing, and the specific gravity had increased to 0·9608 at 12° C.; the iodine absorption had at the same time decreased from the original 85·53 per cent to 64·06 per cent.

Ricinoleic acid assimilates two atoms of bromine or iodine, but does not absorb hydrogen. Nitrous acid transforms it into its stereometrical isomeride—ricinelaïdic acid. On exposure to the

[1] Liebermann and Bellami, *Berichte*, 1887, 962.
[2] Goldsobel, *Berichte*, 1894, 3121; Kasansky, *Journ. f. prakt. Chemie*, 1900 (62), 363.
[3] *Journ. Soc. Chem. Ind.* 1888, 755.
[4] *Journ. Chem. Soc.* 1895, Abstr. i. 500.
[5] *Berichte*, 1894, Ref. 629.
[6] *Ibid.* 1894, 3472.
[7] *Journ. Soc. Chem. Ind.* 1897, 684.

atmosphere ricinoleic acid does not absorb oxygen. By reducing agents, it is converted into stearic acid.

By the action of concentrated sulphuric acid on ricinoleic acid the following products are obtained :[1]—*ricinoleo-sulphuric acid*, $OH . SO_2 . O . C_{17}H_{32} . COOH$, *dihydroxystearo-sulphuric acid*, $OH . SO_2 . O \atop OH$ $>C_{17}H_{33} . COOH$, *dibasic diricinoleic acid*, $O<{C_{17}H_{32} . COOH \atop C_{17}H_{32} . COOH}$, *monobasic diricinoleic acid*, $OH . C_{17}H_{32} . COO . C_{17}H_{32} . COOH$, *dihydroxystearic acid*, $C_{18}H_{36}O_4$, *a solid acid*, $C_{36}H_{70}O_7$, and *isoricinoleic acid*, $C_{18}H_{24}O_3$ (cp. "Turkey-red Oils," chap. xv.).

On oxidising ricinoleic acid with potassium permanganate, two atoms of oxygen are assimilated. *Hazura* and *Grüssner*[2] found that two isomeric trihydroxystearic acids were formed, and concluded, therefore, that the liquid fatty acid of castor oil is a mixture of two isomerides, ricinoleic and *isoricinoleic* acids. This conclusion need not, however, be necessarily adopted, as two stereochemical isomerides may be obtained from one and the same ricinoleic acid.[3]

On treating ricinoleic acid with gaseous hydrobromic acid in the cold, *Kasansky*[4] obtained, according as he varied the conditions of the experiment, monobromo- or dibromostearic acid. On reducing these compounds the ordinary stearic acid was obtained ; hence it is evident that the hydroxyl group in ricinoleic acid has been replaced by bromine. If the substitution of the hydroxyl group be prevented by previous acetylation of the OH group, then an acetylated hydroxystearic acid is ultimately obtained. The hydroxystearic acid resulting from this hydroxylated acid differs from the hitherto known isomerides.

Most of the metallic salts are readily obtained in the crystalline state ; they behave with solvents very much like the corresponding salts of oleic acid. The calcium and barium ricinoleates are soluble in alcohol ; the barium salt, even when repeatedly recrystallised from alcohol, retains water which is not given off even at 120° C. Lead ricinoleate is easily soluble in ether, and melts at 100° C.

The methyl ester of ricinoleic acid has the specific gravity 0·9236, and boils at 245° C. under a pressure of 10 mm. $[\alpha]_D = +3·8$.

The ethyl ester of ricinoleic acid has the specific gravity 0·9145, and boils at 258° under a pressure of 13 mm. $[\alpha]_D = +4·07$.

Ricinelaïdic acid, $\begin{matrix} C_6H_{13} . CH(OH) . CH_2 . CH \\ \| \\ COOH . (CH_2)_7 . CH \end{matrix}$, the stereometric isomeride of ricinoleic acid, is obtained from the latter by the action of nitrous acid. It is optically active ; in a solution of absolute alcohol it gives $[\alpha]_D = +6·67$ $(c = 12)$. Ricinelaïdic acid crystallises in

[1] *Journ. Soc. Chem. Ind.* 1894, 820. An isoricinoleic acid has been described by Juillard ; this acid appears to be a ketonic acid, and is a by-product formed by the action of sulphuric acid on ricinoleic acid ; it is distinguished from ricinoleic acid by its solubility in petroleum ether.

[2] *Ibid.* 1888, 681.

[3] Cp. Mangold, *Berichte*, 1894, Ref. 629.

[4] *Journ. f. prakt. Chem.* 1900 (62), 363.

needles, melting at 52°-53° C. With regard to bromine, iodine, and oxygen absorption, it behaves like ricinoleic acid. On oxidising ricinelaïdic acid with potassium permanganate in alkaline solution two isomerides (most likely stereometric trihydroxylated acids) are formed (*Mangold*).

Ricinic acid has been obtained by *Krafft* on heating barium ricinoleate in a vacuum. The barium salt of ricinic acid remains in the retort; on decomposing it the acid is liberated, which is then purified by fractionating *in vacuo*. The acid forms glistening laminæ (from alcohol), melting at 81° C.; it boils under 15 mm. pressure with very slight decomposition.

A hydroxylated acid $C_{17}H_{32}$ (OH) COOH has been found by *Herrmann*[1] in quince oil; it differs from ricinoleic and its isomeric acids, since its dibromide melts at 180°, whereas ricinoleic and ricinelaïdic dibromides are liquid.

VIII.—Acids of the Series $C_nH_{2n}O_4$, Dihydroxylated Acids

Dihydroxystearic Acid, $C_{18}H_{36}O_4$

The natural dihydroxylated acid occurs, according to *Juillard*,[2] in castor oil to the extent of about 1 per cent, and is prepared from the mixed fatty acids of castor oil by keeping them for some time at a temperature below 12° C. The crystalline magma is drained, pressed, and recrystallised from alcohol, and thus yields a mixture of dihydroxystearic and stearic acids. The latter is removed by washing with hot toluene, and the remaining crude dihydroxystearic acid is recrystallised from boiling alcohol. *H. Meyer*[3] prepares the acid from the lime salts of the mixed castor oil acids by decomposing them with hydrochloric acid, and allowing to crystallise from ether in the cold. After twelve hours' standing crystals of the melting point 140°-141° C. are obtained.

The pure acid melts at 141°-143° C. It is insoluble in ether, petroleum ether, and benzene, slightly soluble in cold toluene, more so in the hot solvent; it dissolves in boiling alcohol and boiling acetic acid. Reducing agents easily convert the acid into stearic acid. By treatment with hydrochloric acid at 180° C., and subsequently with caustic potash, dihydroxystearic acid is converted into the dibasic acid:—COOH . $(HO)C_{17}H_{33}$. O . $C_{17}H_{33}(OH)COOH$.

Probably this acid—being a natural product—is optically active.

The sodium salt forms fine needles.

The methyl- and ethyl-esters melt at 106°-108° C. and 104°-106° C. respectively.

[1] *Arch. der Pharmacie*, 237, 366 (1899). [2] *Journ. Soc. Chem. Ind.* 1895, 811.
[3] *Arch. der Pharm.* 1897, 184; *Chem. Rev.* 1897, 223.

LANOCERIC ACID, $C_{30}H_{60}O_4$

Lanoceric acid has been isolated from the mixture of soaps obtained on saponifying wool wax with alcoholic potash.[1]

The acid crystallises from alcohol in microscopic laminæ; it softens at 102° C. and melts at 104°-105° C.; it then solidifies at 103°-101° C., to melt again at 102° C. It has, however, thereby lost one molecule of water, probably from the two hydroxyl groups, for it still possesses acid properties. Lanoceric acid very readily forms a lactone, *e.g.* when boiled with dilute hydrochloric acid; the lactone melts at 86° C.

Lanoceric acid is almost insoluble in cold water and alcohol, but readily soluble in hot alcohol. It does not combine easily with aqueous potash; a little alcohol, however, readily induces combination. The salt is therefore best prepared in alcoholic solution. The potassium salt behaves exactly like that of lanopalmic acid (p. 116), viz. it dissociates on cooling into the acid salt, which separates, and into free alkali.

IX.—ACIDS OF THE SERIES $C_nH_{2n-2}O_4$, DIBASIC ACIDS

JAPANIC ACID, $C_{22}H_{42}O_4 = C_{20}H_{40}(COOH)_2$

Japanic acid[2] is the first dibasic acid hitherto found to occur in natural fats. It has been detected in small quantities in Japan wax, most likely forming a mixed glyceride together with palmitic acid.

The acid crystallises from alcohol and chloroform in white laminæ, melting at 117·7°-117·9° C. The crystals dissolve but sparingly in most solvents. Japanic acid is heavier than water.

On heating the acid to 200° C. carbon dioxide is given off, and the ketone $\begin{matrix}C_{10}H_{20}\\C_{10}H_{20}\end{matrix}\!\!>\!CO$, melting at 82°-83° C., is obtained.

The potassium salt is sparingly soluble in 95 per cent alcohol; 100 c.c. of this menstruum dissolve 0·1345 grm. at 26° C.

APPENDIX TO THE FATTY ACIDS

The above-described acids occur in natural fats and waxes. Besides these, however, several saturated hydroxylated acids or their inner anhydrides are found in various products of the fat industries. These I describe below, together with some other hydroxylated fatty acids,

[1] Darmstaedter and Lifschütz, *Berichte*, 1896, 1474, 2893; *Journ. Soc. Chem. Ind.* 1896, 548. (The acid is described there as lanocerinic acid.)

[2] Geitel and v. d. Want, *Journ. f. prakt. Chem.* 1900 (61), 151.

which are of great importance for the identification of glycerides of unsaturated acids. These hydroxylated acids are obtained on oxidising unsaturated acids with dilute potassium permanganate in alkaline solution by *Hazura's* method. This method will be fully described below (p. 361).

As the outcome of their own and *Saytzeff's* researches, the following rule has been stated by *Hazura* and *Grüssner*:[1]—All unsaturated fatty acids, when oxidised with potassium permanganate in alkaline solution in the cold, have as many hydroxyl groups added as there are unsaturated carbon atoms in the molecule, yielding thereby saturated hydroxylated acids which contain the same number of carbon atoms in the molecule. Further experiments must decide whether *Hazura's* rule holds good for all unsaturated acids (cp. "Jecoric Acid," p. 115). During the reaction, perhaps owing to the further oxidation of the hydroxylated acids, dibasic acids are also formed; therefore, I shall briefly describe those dibasic acids that have been found amongst the products of oxidation, and are most likely to be met with in similar researches. The following table shows the hydroxylated acids obtained hitherto by this reaction:—

Fatty Acid.	Hydroxylated Acid.
Tiglic acid	(Dihydroxytiglic) tigliceric acid.
(Unknown)	Dihydroxyasellic acid.
Oleic acid	Dihydroxystearic acid.
Elaïdic acid	Dihydroxystearidic acid.
Isooleic acid	Para-dihydroxystearic acid.
(Unknown)	Dihydroxyjecoleic acid.
Ricinoleic acid	{ Trihydroxystearic acid. { α-Isotrihydroxystearic acid.
Ricinelaïdic acid	{ β-Isotrihydroxystearic acid. { γ-Isotrihydroxystearic acid.
Linolic acid	Tetrahydroxystearic (sativic) acid.
Linolenic acid	Hexahydroxystearic (linusic) acid.
Isolinolenic acid (?)	Isolinusic acid.
Erucic acid	Dihydroxybehenic acid.
Brassidic acid	Isodihydroxybehenic acid.
Isoerucic acid	Para-dihydroxybehenic acid.

I.—Hydroxylated Acids

1.—Monohydroxylated Acids

β-Hydroxystearic Acid, $C_{18}H_{36}O_3 = C_{18}H_{35}O_2(OH)$ $= CH_3 . (CH_2)_7 . CH . (OH) . (CH_2)_8 . COOH$[2]

This acid is formed on dissolving ordinary oleic acid or elaïdic acid in concentrated sulphuric acid; simultaneously stearic

[1] *Journ. Soc. Chem. Ind.* 1888, 506.
[2] Shukoff and Schestakoff, *Journ. f. prakt. Chem.* 67 (1903), 415.

acid hydrogen sulphate and stearolactone are formed (see Turkey-red Oils). The glyceride of the same acid is obtained on subjecting triolein, the glyceride of oleic acid, to the same treatment.

β-hydroxystearic acid crystallises in hexagonal plates (from alcohol), melting at 81°-81·5° (*Geitel*), 83°-85° C. (*Saytzeff*), and solidifying at 68°-65°. 100 parts of absolute alcohol dissolve 8·78 parts of the acid at 20° C.; at the same temperature 100 parts of ether dissolve 2·3 parts of the acid.

On heating the acid to 200° C., with or without zinc chloride, a viscous mass is obtained containing the anhydride $C_{18}H_{34}O_2$ and also oleic acid.[1] The hydroxystearic acid is regenerated by boiling the anhydride with caustic potash. On distilling β-hydroxystearic acid in a vacuum, a portion of the acid passes over unchanged, whilst another portion is converted into oleic and isooleic acids. By carefully oxidising β-hydroxystearic acid with chromic acid in acetic acid solution, a ketostearic acid is obtained, whilst sebacic, azelaic, and very small quantities of suberic acid are formed as by-products.

The sodium, zinc, and copper salts are soluble in alcohol; the barium salt is insoluble both in alcohol and ether.

α-Hydroxystearic Acid, $C_{18}H_{36}O_3 = C_{18}H_{35}O_2(OH)$ $= CH_3 . (CH_2)_6 . CH(OH) . CH_2 . (CH_2)_8 . COOH$[2]

On treating isooleic acid with sulphuric acid in the manner already described for ordinary oleic acid, this acid is obtained together with the isomeric β-hydroxystearic acid in varying proportions; these depend on the temperature obtaining during the interaction. The lower the temperature, the larger is the yield of α-hydroxystearic acid. α-hydroxystearic acid is also formed on digesting with silver hydroxide the iodo-stearic acid obtained from isooleic acid and hydriodic acid.

This hydroxystearic acid distils undecomposed under a pressure of 100 mm. (difference from β-hydroxystearic acid), and crystallises (from alcohol) in plates, melting point 77°-79° C., 84°-85° C. (*Hell* and *Sadomsky*).[3] It is more easily soluble in ether than the β-isomeride, whilst less readily soluble in absolute alcohol; 100 parts of the latter dissolve at 20° C. only 0·58 parts of the acid.

On oxidising α-hydroxystearic acid with chromic acid in acetic acid solution, *Shukoff* and *Schestakoff* obtained sebacic acid, a dicarbonic acid, $C_{11}H_{20}O_4$, of the melting point 124° C., and a ketostearic acid, differing from the ketostearic acid prepared from β-hydroxystearic acid by the same method.

[1] It may be pointed out here that the anhydride $C_{18}H_{34}O_2$, being a saturated compound, does not absorb iodine; therefore the oleic acid can be determined quantitatively in the mixture (cp. chap. vi. p. 249).

[2] Shukoff and Schestakoff, *Journ. f. prakt. Chem.* 67 (1903), 417.

[3] *Berichte*, 24, 2392.

(γ-Hydroxystearic Acid, $C_{18}H_{36}O_3 = CH_3 . (CH_2)_{13} . CH(OH) . CH_2 . CH_2 . COOH$)

Stearolactone, $C_{18}H_{34}O_2 = CH_3 . (CH_2)_{13} . CH . CH_2 . CH_2 . CO$ (with O bridging CH and CO)

The free acid has not been prepared yet, its inner anhydride, or lactone, being formed whenever the free acid might be expected. This lactone is obtained when concentrated sulphuric acid acts on ordinary oleic acid[1] (see β-hydroxystearic acid). The lactone is also obtained by heating oleic acid with 10 per cent of zinc chloride to 185° C. (*v. Schmidt's* process, cp. chap. xv.). Stearolactone forms fine white crystalline laminæ, having the melting point 47°-48° C.; it can be distilled almost unchanged. Insoluble in water, it dissolves easily in alcohol, ether, and petroleum ether. Boiling solutions of alkalis dissolve the stearolactone with formation of salts of the γ-hydroxystearic acid. On adding a mineral acid to the solution of any of the salts, stearolactone, but not the acid, is precipitated.

2. Dihydroxylated Acids

(Dihydroxytiglic) Tigliceric Acid,[2] $C_5H_{10}O_4 = C_5H_8O_2(OH)_2$

Tigliceric acid is obtained by oxidising tiglic acid with potassium permanganate. It crystallises in small plates (from ether), melting at 88° C. The acid is very readily soluble in water, alcohol, and acetone, but insoluble in petroleum ether, chloroform, and benzene.

Dihydroxypalmitic Acid, $C_{16}H_{32}O_4 = C_{16}H_{30}O_2(OH)_2$

This acid was obtained synthetically from dibromopalmitic acid (dibromo-addition product of hypogæic acid) by boiling with silver oxide (compare above). It forms small laminæ (from alcohol), melting point 115° C.; they dissolve readily in alcohol and ether.

More recently the same acid was obtained by *Ljubarsky*,[3] on oxidising the liquid fatty acids from Caspian seal oil. This acid seems to form with dihydroxystearic acid a molecular compound behaving in many respects like a chemical individual ("eutectic") of the composition $C_{17}H_{34}O_4$, melting at 124°-125° C.

In the light of *Ljubarsky's* researches the chemical individuality of an acid $C_{17}H_{34}O_4$, described by *Fahrion*,[4] must be doubted.

[1] Cp. Lewkowitsch, *Journ. Soc. Chem. Ind.* 1897, 392.
[2] Fittig, *Liebig's Annalen*, 283. 111.
[3] *Journ. prakt. Chem.* 1898, 26.
[4] *Journ. Soc. Chem. Ind.* 1893, 936. Cp. also *Chem. Zeit.* 1899, 1048. This acid was described in the second edition of this work.

DIHYDROXYSTEARIC ACID,[1] $C_{18}H_{36}O_4 = C_{18}H_{34}O_2(OH)_2$

Dihydroxystearic acid is best prepared by oxidising ordinary oleic acid with potassium permanganate in alkaline solution. It forms crystalline laminæ, melting at 136·5° C. (*Saytzeff*), 134° (*Albitzky*), 132°-133° (*Lewkowitsch*),[2] 131·5°-132° (*Le Sueur*),[3] and solidifying between 119° and 122° C. The acid is completely insoluble in water, easily soluble in hot, less so in cold alcohol, and sparingly soluble in ether.

This dihydroxystearic acid has been split into two optically active isomerides by means of its strychnine salt.[4]

On treatment with potassium permanganate in the hot, pelargonic, azelaic, and oxalic acids are obtained, but not sebacic, suberic, and caprylic acids, as has been stated by *Spiridonoff*.[5]

DIHYDROXYSTEARIDIC ACID, $C_{18}H_{36}O_4 = C_{18}H_{34}O_2(OH)_2$

Elaïdic acid yields this acid on oxidation with potassium permanganate. It differs from the foregoing acid by its lower melting point, viz. 99°-100° C., and by its greater solubility in alcohol. It is also much more easily oxidised in the course of preparation than its isomeride from oleic acid.

p-DIHYDROXYSTEARIC ACID, $C_{18}H_{36}O_4 = C_{18}H_{34}O_2(OH)_2$

This second isomeride of the dihydroxylated stearic acid has been prepared from isooleic acid. It forms a crystalline powder, melting at 79° C., easily soluble in alcohol and ether.

DIHYDROXYJECOLEIC ACID, $C_{19}H_{38}O_4 = C_{19}H_{36}O_2(OH)_2$

This acid is obtained on oxidising the liquid cod liver oil fatty acids with half-saturated solution of potassium permanganate at 0° C.; it melts at 114°-116° C.

DIHYDROXYBEHENIC ACID, $C_{22}H_{44}O_4 = C_{22}H_{42}O_2(OH)_2$

This acid is obtained by oxidising erucic acid with potassium permanganate; it forms granular crystals, melting at 132°-133° C. It dissolves readily in warm alcohol; it is insoluble in cold ether.[6]

[1] This acid must not be confounded with natural dihydroxystearic acid; cp. p. 119.
[2] *Journ. Soc. Chem. Ind.* 1900, 845. [3] *Ibid.* 1901, 1316.
[4] Freundler, *Journ. Chem. Soc.* 1896, Abstr. II. 596.
[5] Cp. Edmed, *Journ. Chem. Soc.* 1898, 627.
[6] Cp. also Albitzky, *Chem. Centr.* 1899, I. 1068.

ISODIHYDROXYBEHENIC ACID,[1] $C_{22}H_{44}O_4 = C_{22}H_{42}O_2(OH)_2$

Isodihydroxybehenic acid is prepared by oxidising brassidic acid with potassium permanganate. The acid melts at 99°-100° C., and solidifies at 88°-87° C.

PARA-DIHYDROXYBEHENIC ACID,[2] β-DIHYDROXYBEHENIC ACID, $C_{22}H_{44}O_4 = C_{22}H_{42}O_2(OH)_2$

This third isomeride is prepared from isoerucic acid; it melts at 86°-88° C., and solidifies at 82°-80° C.

3. Trihydroxystearic Acids, $C_{18}H_{33}O_2(OH)_3$

The acids having this composition have been prepared by oxidising ricinoleic and ricinelaïdic acids. Three acids have been described hitherto by *Hazura* and *Grüssner*;[3] two are derived from ricinoleic, and the third from ricinelaïdic acid. *Mangold* has shown that ricinelaïdic acid also yields two trihydroxylated acids, one of which is certainly identical with that prepared by *Hazura* and *Grüssner*.

TRIHYDROXYSTEARIC ACID, $C_{18}H_{33}O_2(OH)_3$

This acid has been obtained from ricinoleic acid together with the following acid. It crystallises from hot water in microscopic needles; melting at 140°-142° C. It is insoluble in cold, and dissolves with difficulty in hot water, as also in cold alcohol and ether. Warm alcohol and glacial acetic acid dissolve it readily. Trihydroxystearic acid is insoluble in carbon bisulphide, chloroform, benzene, and petroleum ether. Probably this acid is optically active.[4]

α-ISOTRIHYDROXYSTEARIC ACID, $C_{18}H_{33}O_2(OH)_3$

This acid differs from the preceding one by its melting point, 110°-111° C., and by its ready solubility in ether and benzene; it is optically active.[4] $[\alpha]_D = -6{\cdot}25$ in glacial acetic acid ($c = 10$).

β-ISOTRIHYDROXYSTEARIC ACID, $C_{18}H_{33}O_2(OH)_3$

On oxidising ricinelaïdic acid, two isomerides are obtained according to *Mangold*.[5] One acid derived from ricinelaïdic acid has been described by *Hazura* and *Grüssner* as having the melting point 114°-115° C., being sparingly soluble in hot water, ether, chloroform, and petroleum ether, and dissolving readily in alcohol. Probably

[1] Saytzeff, *Journ. prakt. Chem.* 1894 (50), 82; Albitzky, *Chem. Centr.* 1899, I. 1068.
[2] Alexandroff and Saytzeff, *Journ. prakt. Chem.* 1894 (49), 63.
[3] Cp. also Dieff, *ibid.* 1889 (39), 339.
[4] Walden, *Berichte*, 1894, 3475.
[5] *Monatshefte f. Chem.* 1892, 326.

Mangold's acid, of the melting point 113°-116° C., is identical with β-isotrihydroxystearic acid.

The second trihydroxystearic acid from ricinelaïdic acid melts between 117° and 120° C.

It appears very likely that these two acids will rotate the plane of polarised light.

4. Tetrahydroxystearic Acid, $C_{18}H_{32}O_2(OH)_4$

Tetrahydroxystearic or **sativic** acid is obtained on oxidising linolic acid. It crystallises from water in long needles or pyramidal prisms, possessing silky lustre, melting at 173° C. (*Hazura*), 174° (*Hehner* and *Mitchell*). 2000 parts of boiling water dissolve one part of the acid. Sativic acid is insoluble in cold water, ether, chloroform, carbon bisulphide, and benzene. Hot alcohol and glacial acetic acid dissolve it readily. Potassium permanganate oxidises it to azelaic acid.

It is not unlikely that several isomeric tetrahydroxy acids exist, since various observers have obtained a tetrahydroxy acid of lower melting point (152° C.; 165° C.). Besides, *Thoms* obtained from telfairic acid, a hydroxy acid of the melting point 177° C.

5. Hexahydroxystearic Acids, $C_{18}H_{30}O_2(OH)_6$

Linusic Acid,[1] $C_{18}H_{30}O_2(OH)_6$

The linolenic acid contained in drying oils yields on oxidation this hexahydroxylated acid. It crystallises from water as a rule in rhombic plates, sometimes also in needles, melting between 203° and 205° C. Water dissolves it more readily than sativic acid. Linusic acid is insoluble in ether, and sparingly soluble in alcohol.

Isolinusic Acid,[1] $C_{18}H_{30}O_2(OH)_6$

This acid is obtained, together with linusic acid, on oxidising linseed oil fatty acids, hence the existence of isolinolenic acid has been inferred.

Isolinusic acid crystallises in prismatic needles, melting between 173° and 175° C. It is sparingly soluble in cold water, but dissolves easily in hot water and hot alcohol; it is insoluble in ether, benzene, carbon bisulphide, and chloroform.

II.—Dibasic Acids

Acids belonging to this class are met with in the course of the examination of fatty acids obtained by oxidation with potassium permanganate.

[1] Reformatzky doubts the existence of these acids.

These acids are soluble in water, and are therefore easily isolated. Their characteristic melting points afford a ready means for their identification.[1]

Suberic Acid, $C_8H_{14}O_4 = C_6H_{12}(COOH)_2$

Suberic acid crystallises from water in long needles or irregular plates, melting at 140° C.; it boils *in vacuo* at 152·5° C., and under a pressure of 15 mm. at 230° C.

The acid is almost insoluble in chloroform. 100 parts of ether dissolve 0·809 parts at 15° C.; 100 parts of water dissolve at 0°, 15·5°, 20°, 50°, 65°—0·08, 0·142, 0·16, 0·98, 2·2 parts respectively.

Azelaic Acid, $C_9H_{16}O_4 = C_7H_{14}(COOH)_2$

This acid crystallises from water in large laminæ or long flat needles, melting at 106·2° C.; it boils *in vacuo* at 158° C., and under a pressure of 15 mm. at 237° C.

100 parts of ether dissolve at 11° 1·88 parts, and at 15° C. 2·68 parts of the acid. 100 parts of water dissolve at 0°, 20°, 50°, 65°—0·10, 0·24, 0·82, 2·22 parts respectively.

Sebacic Acid, $C_{10}H_{18}O_4 = C_8H_{16}(COOH)_2$

Sebacic acid crystallises from water in thin laminæ. It melts at 133-133·5° C., and boils *in vacuo* at 164° C., and under a pressure of 15 mm. at 243·5° C. The acid is easily soluble in alcohol and ether. 100 parts of water dissolve at 0°, 20°, 50°, 65° C.—0·004, 0·10, 0·22, 0·42 parts respectively.

B. ALCOHOLS

I.—Alcohols of the Ethane Series, $C_nH_{2n+2}O$

The alcohols belonging to this series occur in waxes, or in the wax-like constituents of some fats, and are solid, white, crystallisable substances, melting without decomposition. They are not acted upon by dilute alkalis or acids; on boiling with alcoholic potash and diluting the solution with water, they are precipitated unchanged. Hence they are termed "unsaponifiable."

On heating the alcohols with organic acids, or their chlorides, or anhydrides, combination takes place with separation of water, esters being formed; thus on heating cetyl alcohol with acetic acid in presence of sulphuric acid, cetyl acetate is obtained, as explained by the following equation:—

$$C_{16}H_{33}.OH + CH_3.CO.OH = H_2O + C_{16}H_{33}.O.CO.CH_3.$$

[1] Cp. Bouveault, *Bull. Soc. Chim.* 1898, 562.

The alcohols dissolve in concentrated sulphuric acid in the cold, forming alkyl sulphuric acids; on boiling with dilute acids they are again resolved into their components.

A characteristic property of the alcohols, which can be made use of for their identification, is their behaviour with soda-lime on heating; they are thereby converted into the corresponding fatty acids, with evolution of hydrogen. Thus cetyl alcohol yields palmitic acid, as indicated by the equation—

$$C_{15}H_{31}.CH_2.OH + NaOH = C_{15}H_{31}.COONa + 2H_2.$$

These reactions have been employed for the quantitative determination of these alcohols, as will be detailed below (chap. ix. p. 380).

Pisangceryl Alcohol, $C_{13}H_{28}O$ [1]

Pisangceryl alcohol is the alcoholic constituent of pisang wax; it melts at 78° C.

Cetyl Alcohol, $C_{16}H_{34}O$

Cetyl alcohol, or ethal, occurs, combined with palmitic acid, in spermaceti. The alcohol has also been found in the sebaceous glands of geese and ducks.

Cetyl alcohol is a white, tasteless, and odourless crystalline mass, melting at 50° C., and boiling at 344° C., without decomposition, at the ordinary pressure; under a pressure of 15 mm. it boils at 189·5° C., *in vacuo* at 119° C. The specific gravity at $\frac{49·5°}{4°}$ C. is 0·8176; at $\frac{60°}{4°}$ C. 0·8105; at $\frac{79·7°}{4°}$ C. 0·7984; and at $\frac{98·7°}{4°}$ C. 0·7837.

Cetyl alcohol is insoluble in water, but dissolves in alcohol, and is very easily soluble in ether and benzene. The statement that cetyl alcohol, when heated with potassium bichromate and dilute sulphuric acid, is converted into cetyl aldehyde crystallising from alcohol and ether in lustrous laminæ is incorrect, cetyl alcohol remaining for the most part unchanged when oxidised in aqueous solution; in acetic acid solution the oxidising mixture yields palmitic acid.[2] Cetyl alcohol dissolves in cold concentrated sulphuric acid to form cetyl sulphuric acid, $C_{16}H_{33}O.SO_3H$; on boiling this product with aqueous hydrochloric acid the alcohol is regenerated.[3]

Cetyl acetate crystallises in needles, melting from 22°-23° C., and boiling at 199·5°-200·5° C. under a pressure of 15 mm. It dissolves sparingly in alcohol.

Cetyl benzoate crystallises in scales, melting at 30° C.; it is readily soluble in ether, but dissolves with difficulty in alcohol.

[1] Greshoff and Sack, *Rec. des Trav. Chim. des Pays-Bas*, 1901, 65.
[2] Cp. Claus and v. Dreden, *Journ. f. prakt. Chem.* 1891 (43), 148.
[3] Cochenhausen, *Dingl. Polyt. Journ.* 1897 (303), 284.

OCTODECYL ALCOHOL, $C_{18}H_{38}O$

This alcohol also occurs, as an ester, in spermaceti. It crystallises in large silvery laminæ (from alcohol), melting at 59° C., and boiling at 210·5° C. under 15 mm. pressure. It undergoes decomposition even when distilled under a pressure of 100 mm. The specific gravity is 0·8124 at $\frac{59°}{4°}$ C., 0·8048 at $\frac{70°}{4°}$ C., and 0·7849 at $\frac{99·1°}{4°}$ C.

Octodecyl acetate melts at 31° C., and boils at 222°-223° C. under a pressure of 15 mm.

CARNAÜBYL ALCOHOL, $C_{24}H_{50}O$

Carnaübyl alcohol occurs in wool wax;[1] from its alcoholic solution (in 75 to 80 per cent alcohol) crystals are obtained melting at 68°-69° C., solidifying at 67°-65° C. The alcohol very tenaciously retains water and forms a tallow-like mass, consisting of 26·7 per cent of carnaübyl alcohol, and 73·3 per cent of water. On exposure to the air this mass does not lose its weight.

On oxidising the alcohol with chromic acid, carnaübic acid is obtained.

An alcohol of the formula, $C_{24}H_{50}O$ or $C_{25}H_{52}O$, has been found in small quantities in beeswax.

CERYL ALCOHOL, $C_{26}H_{54}O$

Ceryl alcohol occurs as ceryl cerotate in Chinese wax, and as ceryl palmitate in opium wax; in wool fat it occurs in the free state,[2] and perhaps also as ceryl cerotate.[3] It has also been identified as a constituent of the wax of flax[4] and of carnaüba wax.

From its alcoholic solution, crystals are easily obtained, which melt at 79° C.; they cannot be distilled unchanged. On heating ceryl alcohol with soda-lime, cerotic acid is obtained.

Ceryl alcohol behaves with concentrated sulphuric acid like cetyl alcohol.

Ceryl acetate melts at 65° C.

ISOCERYL ALCOHOL, $C_{27}H_{56}O$

This alcohol has been found in the wax of *Ficus gummiflua*. The alcohol melts at 62° C.; its acetate at 57° C. An alcohol,[5] of the formula $C_{27}H_{56}O + 6H_2O$, has been isolated from wool fat.

[1] Darmstaedter and Lifschütz, *Berichte*, 1896 (29), 2890; *Journ. Soc. Chem. Ind.* 1897, 150.
[2] Lewkowitsch, *Journ. Soc. Chem. Ind.* 1892, 138.
[3] Buisine, *Bull. Soc. Chim.* 1887 (72), 201.
[4] Cross and Bevan, *Journ. Chem. Soc.* 1890, 196.
[5] Darmstaedter and Lifschütz, *Berichte*, 29, 2895.

MYRICYL ALCOHOL (Melissyl Alcohol), $C_{30}H_{62}O$ ($C_{31}H_{64}O$)

Myricyl alcohol occurs as palmitate in beeswax, this ester forming that part of beeswax which is insoluble in alcohol (*Brodie*). In the free state and in combination with acids it has been found in carnaüba wax. It crystallises in small needles possessing silky lustre and melting at 85° C. or 88° C. (*Gascard*). It may be partly distilled unchanged. Nearly insoluble in cold, it dissolves readily in hot alcohol. Heated with soda-lime, it is converted into melissic acid. According to *Schwalb*,[1] myricyl alcohol from beeswax has the formula $C_{31}H_{64}O$. *Gascard*[2] states that the myricyl alcohols from beeswax and carnaüba wax are identical, and have the composition expressed by the formula $C_{31}H_{64}O$.

Myricyl acetate melts at 70° C.

PSYLLOSTEARYLIC ALCOHOL, $C_{33}H_{68}O$[3]

This alcohol, described at first as having the composition $C_{33}H_{66}O$, later on considered to be an anhydride of the formula $(C_{33}H_{66}O)_2$, has been definitely recognised as an alcohol having the composition expressed by the formula $C_{33}H_{68}O$. The alcohol occurs combined with psyllostearylic acid (psyllic acid) as a wax, produced by the aphide *Psylla Alni* (living on the leaves of *Alnus incana*).

The alcohol is obtained by saponifying the wax, and crystallises from benzene, petroleum ether, and chloroform in scales of silky lustre. It melts at 68°-70° C.

Psyllostearyl benzoate, $C_{33}H_{67}.O.C_7H_5O$, crystallises from benzene or petroleum ether in needles, melting at 68°-69° C.

II.—ALCOHOLS OF THE ALLYLIC SERIES,[4] $C_nH_{2n}O$

The alcohols belonging to this group have not yet been studied thoroughly; it is noteworthy that they, like the alcohols of the preceding and the following two groups, occur in waxes.

LANOLIN ALCOHOL, $C_{12}H_{24}O$

This alcohol has been stated by *Marchetti*[5] to occur in wool wax; shortly afterwards *Darmstaedter* and *Lifschütz*[6] described two more alcohols of the formula $C_{10}H_{20}O$ and $C_{11}H_{22}O$, also isolated from wool wax. The latter chemists, believing to have discovered the lower homologues, proposed the name "Lanestols" for these alcohols, but more accurate examination undertaken by them in consequence

[1] *Liebig's Annalen*, 235, 126.
[2] *Journ. Soc. Chem. Ind.* 1893, 955.
[3] Sundwick, *Zeit. Physiolog. Chem.* 1901 (32), 355.
[4] Most likely the unsaturated alcohols occurring in sperm oil (Lewkowitsch, *Journ. Soc. Chem. Ind.* 1892, 134) belong to this series.
[5] *Gazz. Chimica*, 1895, 22.
[6] *Journ. Soc. Chem. Ind.* 1896, 206.

of *Lewkowitsch's* researches [1] proved that these two alcohols $C_{10}H_{20}O$ and $C_{11}H_{22}O$ do not exist in wool wax. Therefore also the existence of *Marchetti's* alcohol becomes doubtful.

An alcohol, having the composition $C_{15}H_{30}O$, has been found in the ether-soluble part of the wax of *Ficus gummiflua*. Another alcohol of the formula $C_{36}H_{72}O$ is said to occur, combined with acids, in the wax of cochineal.

III.—Alcohols of the Series $C_nH_{2n-6}O$

Ficoceryl Alcohol, $C_{17}H_{28}O$ [2]

Ficoceryl alcohol is the alcoholic constituent of gondang wax; it melts at 198° C.

IV.—Alcohols of the Glycolic Series, $C_nH_{2n+2}O_2$

An alcohol of the composition $C_{25}H_{52}O_2 = C_{23}H_{46}\langle{}^{CH_2 . OH}_{CH_2 . OH}$ occurs, according to *Stürcke*,[3] in carnaüba wax, combined with acids. This alcohol forms a crystalline powder, melting at 103·5°-103·8° C.; it dissolves sparingly in boiling petroleum ether, and somewhat more readily in ether and in benzene. On heating with soda-lime, a dibasic acid, $C_{23}H_{46}\langle{}^{COOH}_{COOH}$, is obtained.

Cocceryl Alcohol, $C_{30}H_{62}O_2$

The wax of cochineal contains the coccerate of this alcohol. The alcohol is a crystalline powder (from alcohol), melting between 101° and 104° C. On oxidising it with chromic acid in acetic acid solution, pentadecylic acid, $C_{15}H_{30}O_2$, is obtained.

V.—Alcohols of the Series $C_nH_{2n+2}O_3$

Glycerol, $C_3H_8O_3 = CH_2(OH) . CH(OH) . CH_2(OH)$

Glycerol occurs in combination with fatty acids in all fats and fatty oils. Its synthetical preparation has therefore only theoretical interest. Pure glycerol is a colourless, odourless, viscid liquid, having a sweet taste and possessing neutral reaction. On exposure to an intense cold for a prolonged time, it crystallises in rhombic crystals,

[1] *Journ. Soc. Chem. Ind.* 1896, 15.
[2] Gresshoff and Sack, *Rec. des Trav. Chim. des Pays-Bas*, 1901, 65.
[3] *Liebig's Annalen*, 228, 283.

melting at 20° C. With the help of a few crystals of glycerol, large quantities can easily be converted into crystals at the freezing point of water.

Glycerol is oily to the touch, and produces on the skin, and especially on the mucous membrane, the sensation of heat, due to its absorbing moisture from the tissues. The water absorbing power of glycerol is so great that on exposure, as much as 50 per cent of its own weight of water is taken up from the atmosphere.

The specific gravity of pure glycerol has been determined by several observers, whose statements do not agree, owing no doubt to the difficulty of freeing it from the last traces of water. The most reliable values are the following:—1·26468 at $\frac{15°}{15°}$ C., 1·2620 at $\frac{17·5°}{17·5°}$ C.; further information will be given in Chapter XV., where the numbers for the refractive index will also be found.

Pure glycerol boils under 760 mm. pressure at 290° C., with slight decomposition. Under a pressure of 50 mm. it boils at 210° C., and under 12·5 mm. at 179·5° C. In a vacuum it distils unchanged.

Heated slowly in a dish to 150°-160° C. pure glycerol evaporates without leaving any residue. At 150° C. it burns with a blue flame without emitting odour. When it is heated rapidly, especially in a platinum dish, it burns with production of acroleïn, yielding at the same time a residue consisting of polyglycerols.

At the ordinary temperature glycerol does not volatilise; at the boiling point of water, however, appreciable quantities may escape. Thus if glycerol be heated in an open dish on a water-bath, a slight loss will be incurred, such loss depending on the shape of the vessel (whether deep or shallow), the area of the surface exposed,[1] and the frequency with which the air resting on the surface is renewed. Glycerol can be completely freed from water by allowing it to stand *in vacuo* over sulphuric acid.[2]

Glycerol is miscible with water in all proportions; on mixing glycerol with water, a contraction of volume and an increase of the temperature takes place. The greatest increase of temperature occurs on mixing 58 parts of glycerol (by weight) with 42 parts of water, and amounts to 5° C.; the greatest contraction equals 1·1 per cent (*Gerlach*). A dilute solution may be boiled without loss of glycerol, until a concentration of 70 per cent is reached.[3] If the boiling be continued, glycerol volatilises with the water vapours. Tables of specific gravities of dilute solutions will be found in Chapter XV.

Glycerol is also miscible in all proportions with alcohol; it dissolves easily in a mixture of alcohol and ether, but is sparingly soluble in the latter solvent alone, one part of glycerol, specific gravity 1·23, requiring about 500 parts of ether. It is therefore impossible to extract glycerol from its aqueous solution by means of ether.

[1] Nessler and Barth, *Berichte*, 1884 (17), Ref. 543.
[2] Clausnitzer, *Zeit. f. analyt. Chemie*, 20, 65. [3] Hehner, *Analyst*, 1887, 65.

Nine parts of glycerol are soluble in 100 parts of ethyl acetate. Glycerol is insoluble in chloroform, petroleum ether, carbon bisulphide, and benzene; it is also insoluble in oils and fats (*Lewkowitsch*).

In concentrated sulphuric acid glycerol dissolves to form glycerosulphuric acid, $C_3H_7O_3 . SO_3H$, which is dissociated into glycerol and sulphuric acid on boiling with dilute acids.

Glycerol possesses powerful solvent properties, combining in this respect the properties of water and alcohol; many substances dissolve even more easily in it than in either of the two liquids. The following table of solubilities will serve to illustrate this:—

100 parts of glycerol dissolve	98	parts of crystal soda.
	60	,, ,, borax.
	50·5	,, ,, potassium arsenate.
	50	,, ,, sodium arsenate.
	50	,, ,, zinc chloride.
	40	,, ,, alum.
	40	,, ,, potassium iodide.
	30	,, ,, copper sulphate.
	25	,, ,, ferrous sulphate.
	25	,, ,, potassium bromide.
	20	,, ,, lead acetate.
	20	,, ,, ammonium carbonate.
	20	,, ,, arsenious acid.
	20	,, ,, arsenic acid.
	20	,, ,, ammonium chloride.
	15	,, ,, oxalic acid.
	10	,, ,, barium chloride.
	10	,, ,, copper acetate.
	8	,, ,, sodium carbonate.
	7·5	,, ,, mercury bichloride.
	5	,, ,, calcium sulphide.
	3·5	,, ,, potassium chlorate.
	1·9	,, ,, iodine.
	about 1	part of calcium sulphate.
	0·1	,, ,, sulphur.

An aqueous glycerol solution, specific gravity 1·114, dissolves 0·957 per cent of calcium sulphate.

Metallic soaps (which are insoluble in water) are to some extent dissolved by glycerol; thus—

100 parts of glycerol, sp. gr. 1·114, dissolve	0·71	parts of iron oleate.
	0·94	,, ,, magnesium oleate.
	1·18	,, ,, calcium oleate.

Metallic Glyceroxides

Glycerol dissolves caustic alkalis, alkaline earths, and lead oxide to form chemical compounds with them. Lime, strontia, and baryta are precipitated nearly completely from such solutions by carbon dioxide, a small quantity only of the earths escaping precipitation. In presence of caustic alkalis, glycerol also dissolves ferric oxide,

cupric oxide, and bismuth oxide, no doubt owing to the formation of soluble compounds, such as are represented by monosodium-cupro-glyceroxide (see below). The oxides named are not reduced to metal, or at most only to the lower oxides. However, the following oxides, silver oxide (cp. below, p. 138), gold oxide, mercury oxide, rhodium oxide, palladium oxide, and platinum oxide (Ag_2O, Au_2O_3, HgO, RhO_2, PdO, PtO_2), *are reduced on heating with alkaline glycerol* solution to metals (*Bullnheimer*).[1]

The following glyceroxides have been prepared in a pure state:—

Monosodium glyceroxide, $NaC_3H_7O_3$, is obtained on mixing a solution of metallic sodium in absolute alcohol, *i.e.* sodium ethoxide, with glycerol. A precipitate is formed consisting of extremely deliquescent, rhombic crystals having the formula $NaC_3H_7O_3 + C_2H_6O$. On heating to 100° C., the molecule of alcohol escapes, leaving behind the monosodium glyceroxide as a white, highly hygroscopic powder, which is converted by water into glycerol and caustic soda. If, in the preparation of monosodium glyceroxide, sodium methoxide be used, the crystalline compound has the composition :—$NaC_3H_7O_3 + CH_4O$.

Disodium glyceroxide, $Na_2C_3H_6O_3$.—This compound is prepared by triturating the crystals of monosodium glyceroxide with one molecule of sodium ethoxide under absolute alcohol, and boiling the mixture for several hours.

The potassium derivatives correspond completely to those of sodium just described.

Calcium glyceroxide, $CaC_3H_6O_3$, is a crystalline powder obtained by heating 14 parts of calcium oxide with 23 parts of anhydrous glycerol to 100° C., and cooling the mixture as soon as a violent reaction sets in. Water decomposes it into calcium oxide and glycerol.

Barium glyceroxide, $BaC_3H_6O_3$, is a deliquescent powder. It is prepared by warming 67·1 parts of anhydrous glycerol with 100 parts of baryta to 70° C. Hot water decomposes it rapidly into glycerol and baryta; cold water acts but slowly on it.

Monoplumbo-glyceroxide, $PbC_3H_6O_3$, is prepared by adding 500 grms. of lead hydroxide (obtained by pouring a warm solution of lead nitrate into a large excess of warm ammonia and drying the precipitate on the water bath) to 1000 grms. of boiling glycerol (85 per cent) with constant stirring. The mass is cooled down to 0° C., and finally 2500 c.c. of alcohol are added at 0° C.[2] The monoplumbo-glyceroxide thus prepared contains a little nitric acid, and very likely has the composition $2Pb.C_3H_5O_3, Pb(NO)_3 + (OH)Pb(NO_3)$. A product free from nitric acid is obtained by *Morawski's* method :—Dissolve 22 grms. of lead acetate in 250 c.c. of water, add 20 grms. of glycerol, heat and pour into the boiling solution a concentrated solution of 15 grms. of potassium hydrate. A slight precipitate is filtered off, and the filtrate allowed to crystallise; in the course of a couple

[1] *Forschungsber. über Lebensmittel*, etc. 4, pp. 12, 31.
[2] Fischer and Tafel, *Berichte*, 1888, 2635.

of days a large quantity of fine white needles, the monoplumboglyceroxide, separate.

If basic lead acetate is used instead of sugar of lead, basic plumboglyceroxides are obtained of the composition $Pb_3(C_3H_5O_3)_2$ and $4PbC_3H_6O_3 . PbO$.

Disodium-mangano-glyceroxide, $Na_2(C_3H_5O_3)_2Mn$.—This compound is prepared by boiling anhydrous glycerol with 1·1 parts of caustic soda (spec. gravity 1·38) to which 4 parts of freshly precipitated hydrated manganese peroxide have been added.

Monosodium-cupro-glyceroxide[1] is prepared by placing 5 grms. of cupric hydrate, $Cu(OH)_2$, 15 c.c. water, 2·5-3 grms. glycerol, and 3 grms. solid caustic soda in a flask until the caustic soda is dissolved, then adding 50 c.c. of 96 per cent alcohol, filtering off, and again adding alcohol until a distinct turbidity is noticed. After 6 to 10 hours' standing, fine blue needles separate, having the formula $(NaCuC_3H_5O_3)_2 + C_2H_5OH + 9H_2O$. On drying the crystals *in vacuo* at 100° C. the alcohol and 3 molecules of water are given off, leaving behind $(NaCuC_3H_5O_3)_2 + 6H_2O$. If copper nitrate be employed, hexagonal plates of the composition $(NaCuC_3H_5O_3) + 3H_2O$ are obtained; these crystals are only formed in presence of a certain quantity of sodium nitrate.

Monolithium-cupro-glyceroxide,[2] $LiCuC_3H_5O_3 + 6H_2O$, forms blue hexagonal plates.

Esters of Glycerol

Glycerol, possessing the properties of a weak base, combines also with acid radicles to form esters. The most important esters are those resulting from the combination of glycerol with fatty acids, viz. the glycerides, or the natural oils and fats. Of the esters formed by the combination of inorganic acid radicles and glycerol, but two need be mentioned here, glycyl trinitrate and glycyl arsenite, both being used in the arts, especially the former, which is manufactured on an extensive scale, and forms the main outlet for the large quantities of glycerol that are produced commercially.

Glycyl trinitrate, Nitroglycerin, $C_3H_5(O . NO_2)_3$, is prepared by allowing glycerol to run into a mixture of one part of strongest nitric acid and two parts (by weight) of concentrated sulphuric acid. It is a heavy oily liquid of specific gravity 1·600. Its most remarkable property is that of exploding violently under certain conditions. Nitroglycerin forms the chief ingredient of almost all modern "high explosives" and "smokeless powders." Thus dynamite is produced by mixing nitroglycerin with kieselguhr, whilst "blasting gelatin" is prepared by dissolving nitrocellulose in nitroglycerin.

Glycyl arsenite, $C_3H_5AsO_3$, is formed by dissolving arsenious oxide in glycerol. It is a butter-like substance, melting at 50° C. to a thick liquid. It decomposes above 250° C., but is volatile with the vapours of glycerol. It has not yet been ascertained whether on

[1] *Berichte*, 1898, 1453. [2] *Ibid.*

distillation in a current of superheated steam, the arsenite is volatilised together with glycerol, or whether the arsenite is hydrolysed by the steam. At any rate, arsenious acid is found in the distillate.[1] Glycyl arsenite is used in calico-printing.

Reactions of Glycerol

The most characteristic reaction of glycerol is the penetrating smell of acroleïn which it emits when heated rapidly. The same smell is noticed when glycerides are burnt, as, *e.g.*, when an oil-lamp or a tallow candle has been blown out. The formation of acroleïn is observed most distinctly when the glycerol is mixed with dehydrating substances, such as (twice its weight of) hydrogen potassium sulphate. The acroleïn is formed according to the following equation :—

$$C_3H_8O_3 = C_3H_4O + 2H_2O.$$

Acroleïn is a liquid, possessing a most penetrating odour; its vapours affect the eyes intensely, causing a copious flow of tears. It is readily soluble in water, boils at 42·4° C., and is easily converted into a resinous mass on exposure to the air. The most delicate reagents for detecting acroleïn in aqueous solutions are:—an ammoniacal solution of silver nitrate (reduction to metallic silver with production of a mirror) and *Schiff's* reagent, a solution of rosaniline which has been decolourised by sulphur dioxide (restoration of the pink colour of decolourised rosaniline). The latter reaction, however, is less delicate than the silver test.

If the quantity of glycerol under examination is very small some uncertainty may arise owing to the evolution of sulphurous acid, of vapours of sulphuric acid, and of empyreumatic substances. Hence *Kohn*[2] recommends the isolation of the acroleïn formed. This is best done in the manner proposed by *Grünhut*[3]:—The substance is mixed in a flask with double its weight of finely powdered potassium bisulphate, the flask is closed by a perforated cork fitted with a suitably bent tube, so that the gases escaping on heating the flask in a sand bath can be condensed in a test-tube immersed in a freezing mixture. In the presence of glycerol the condensate in the test-tube will smell distinctly of acroleïn. A confirmatory test is to add to the contents of the test-tube a few drops of a solution containing 3 grms. of silver nitrate in 30 grms. of ammonia of the specific gravity 0·923, previously mixed with a solution of 3 grms. of caustic soda in 30 grms. of water. The silver mirror must then be obtained in the cold.

A very sensitive colour reaction for acroleïn has been recommended by *Lewin*:[4]—Prepare a solution of piperidin in sodium nitroprusside and add acroleïn. In a dilution of 1 : 100 a gentian blue

[1] Lewkowitsch, *Year Book of Pharmacy*, 1890, 380.
[2] *Journ. Soc. Chem. Ind.* 1899, 148.
[3] *Zeit. f. analyt. Chem.* 1899, 41.
[4] *Berichte*, 1899, 3388.

colouration is obtained, and in a dilution of 1 : 1000 a pure blue. The blue colouration is still noticeable in a dilution of 1 : 2000.

A borax bead moistened with glycerol or a dilute glycerol solution gives a green colouration by the flame test. This reaction, however, cannot be considered a characteristic one, as it is a general reaction of alcohols. If glycerol be added to a cold solution of borax, made pink by addition of phenolphthalein, the colouration disappears. On heating, the pink colour reappears, to disappear again on cooling. This reaction cannot be used for the detection of glycerol, as considerable quantities of glycerol are required to discharge the pink colour of a borax solution.

On adding potassium permanganate to a solution of glycerol which has been acidulated with sulphuric acid, decolouration takes place, but very slowly. Even on boiling, the glycerol only undergoes complete oxidation with difficulty. Experiments made by *Lenz*[1] have shown that on boiling an acidulated solution of glycerol with an excess of a 1 per cent solution of potassium permanganate, no more than 34 per cent of the quantity required for complete oxidation is reduced. Only by a large excess of concentrated permanganate solution can glycerol be oxidised to carbonic acid. *Campani* and *Bizarri* state that on oxidising glycerol with potassium permanganate in alkaline solution, the following products are obtained :—carbonic anhydride, formic, acetic, propionic, and oxalic acids, and also small quantities of tartronic acid. If, however, the oxidation in alkaline solution is carried out according to the directions given by *Benedikt* and *Zsigmondy* (see "Quantitative Estimation of Glycerol," chap. vi. p. 283), the glycerol is completely converted into oxalic and carbonic acids according to the following equation :—

$$C_3H_8O_3 + 2K_2Mn_2O_8 = K_2C_2O_4 + K_2CO_3 + 4MnO_2 + 4H_2O.$$

Glycerol is completely oxidised to carbonic anhydride and water by treatment with potassium bichromate and sulphuric acid, as indicated by the following equation :—

$$3C_3H_8O_3 + 7Cr_2O_7K_2 + 28SO_4H_2 = 7[Cr_2(SO_4)_3 + SO_4K_2] + 9CO_2 + 40H_2O$$

which is expressed in a simpler form thus—

$$2C_3H_8O_3 + 7O_2 = 6CO_2 + 8H_2O.$$

Dry potassium permanganate reacts violently with concentrated glycerol. If finely powdered potassium permanganate be heaped up to a small truncated cone, and concentrated glycerol be poured into a hole made on the top, after a very short time fumes escape, the glycerol commences to froth, and ignites spontaneously with violent evolution of gases.[2]

Fehling's solution is slightly reduced by glycerol if diluted with but little water. On boiling this solution for ten minutes, and allowing to stand for 24 to 48 hours, a red or a yellow precipitate is

[1] *Journ. Soc. Chem. Ind.* 1885, 368. [2] Dvorak, *Chem. Zeit.*, 1902, 903.

obtained. If, however, the glycerol be diluted with ten times its bulk of water no reduction occurs.

At the temperature of boiling water, a mixture of glycerol and silver nitrate solution gives on addition of a few drops of ammonia a precipitate of metallic silver. If an excess of ammonia be mixed with the glycerol in the cold, and then heat applied, as a rule no reduction takes place on addition of silver nitrate, simply because the glycerol has not been heated sufficiently ; the addition of caustic soda or potash, however, causes metallic silver to separate slowly. According to *Bullnheimer*[1] 1 part of metallic silver corresponds to 11·3 parts of glycerol.

Methods for the quantitative determination of glycerol will be described in Chapter VI. All these methods are indirect methods. With a view to determining the glycerol in a direct manner by isolating a derivative of glycerol which would permit its quantitative determination, *Niemilowicz*[2] has studied the action of hydrobromic acid on a solution of glycerol in concentrated sulphuric acid. There are, however, two products formed: tribromopropaldehyde and tribromopropionic acid.

On heating glycerol with hydriodic acid, without using an excess of the latter, allyliodide and propylene are formed. In the presence of an excess of hydriodic acid, also isopropyliodide is obtained with smaller quantities of propylene, these quantities varying according to the conditions of the experiment. *Zeisel* and *Fanto*[3] have shown that glycerol can be converted quantitatively into isopropyliodide, if an excess of strong hydriodic acid, specific gravity 1·7, be used. This has been made the basis for a quantitative determination of pure glycerol, by distilling the isopropyliodide formed into an alcoholic solution of silver nitrate (cp. chap. vi.).

V.—Alcohols of the Aromatic Series

Cholesterol, $C_{26}H_{44}O$ ($C_{27}H_{44}O$?)

Cholesterol occurs in considerable quantities in wool fat, a product consisting chiefly of cholesteryl and isocholesteryl esters. It is also found in human bile, the biliary calculi being almost wholly composed of cholesterol. It is frequently met with in the animal organism, its presence having been proved in blood, in the brain, in hair, in the epidermis, in the yolk of eggs, in the testicles, and in various morbid products of the animal body—*e.g.* the hydropic liquid of the stomach, ovarian tumours, etc. Since all animal oils and fats contain small quantities of cholesterol, the presence of cholesterol in an oil or fat points to an animal origin. The quantity

[1] *Forschungsb. Lebensmittel, Hyg., forens. Chemie*, 1897 (4), 12 ; *Chem. Ztg.* 1897, Repert. 76.

[2] *Journ. Chem. Soc.* 1890, Abstr. 861.

[3] *Zeit. f. d. landw. Versuchsw. in Oesterr.* 1902, 1.

of cholesterol in the oils and fats varies from 0·2 to about 1·0 per cent. The liver oils only seem to contain somewhat larger proportions.

The chemical formula of cholesterol has not yet been established with certainty. *Reinitzer*[1] is of the opinion that three homologues of cholesterol exist, and that the formula may, therefore, vary according to the source of cholesterol. The three homologues have, in his opinion, the formulæ $C_{25}H_{42}O$, $C_{26}H_{44}O$, and $C_{27}H_{46}O$. Cholesterol prepared from biliary calculi has the composition $C_{27}H_{46}O$. *Mauthner* and *Suida* favour the formula $C_{27}H_{44}O$; *Walitzki*, however, prefers the formula $C_{27}H_{46}O$.

Cholesterol crystallises from chloroform in anhydrous needles (cp. p. 141, "Phytosterol"), having the specific gravity 1·067, and melting point 148·4-150·8° C. (corr. *Bömer*). Carefully heated under ordinary pressure, it volatilises undecomposed; it is, however, best distilled in a vacuum. From its hot alcoholic solution it crystallises in laminæ (cp. p. 141), containing one molecule of water which evaporates on standing over sulphuric acid, but more quickly on drying the crystals at a temperature of 100° C. Cholesterol is insoluble in water, and very sparingly soluble in cold dilute alcohol. It dissolves in 9 parts of boiling alcohol, specific gravity 0·87, and in 5·55 parts of boiling alcohol, specific gravity 0·83. Ether, carbon bisulphide, and chloroform dissolve it easily, less readily so petroleum ether. According to *Bömer*,[2] 100 c.c. of petroleum ether (specific gravity 0·7522, boiling point 35°-85° C.) dissolve at 19° C. 0·8320 grm., and at 23° C. 1·0380 grms.

Cholesterol is lævo-rotatory. *Hesse* found for the specific rotation in ethereal and chloroformic solutions, at 15° C.:—$[\alpha]_D = -31·12$ and $[\alpha]_D = -(36·61 + 0·249c)$ for $c = 2$ to 8 grms. respectively.

On adding bromine to a solution of cholesterol in carbon bisulphide, a bromo-addition product, cholesterol dibromide, $C_{26}H_{44}O . Br_2$, is formed. With iodo-chloride an iodo-chloro-addition product is obtained;[3] cholesterol may thus be estimated quantitatively (chap. ix. p. 379). If only half of the theoretical quantity of bromine be added, crystals having the following composition, $C_{26}H_{44}OBr_2 + C_{26}H_{44}O$, separate.[4]

Cholesterol dissolves in concentrated sulphuric acid; on warming the mixture, it is converted into a hydrocarbon $C_{26}H_{42}$ (?)—cholesterilen[5] (difference from aliphatic alcohols). As a further important difference from aliphatic alcohols, it should be noted that on heating cholesterol with soda lime[6] no fatty acids are formed. On heating cholesterol with normal alcoholic potash on the water-bath under a reflux condenser for 3 to 4 hours, 20 to 25 per cent of a hydrated

[1] *Journ. Soc. Chem. Ind.* 1888, 585. Cp. *Jahrbuch der Chemie*, 1896, 360.
[2] *Zeit. f. Unters. der Nahrgs. und Genussm.* 1898, 37. *Journ. Soc. Chem. Ind.* 1898.
[3] Lewkowitsch, *Journ. Soc. Chem. Ind.* 1892, 43.
[4] Cloëz, *Chem. Ztg.* 1897, 354.
[5] Zwenger, *Annalen*, 66, 5; 69, 347; Mauthner and Suida, *Monatshefte*, 17, 33; cp. also Cochenhausen, *Dingl. Polyt. Journ.* 1897 (303) 284.
[6] Lewkowitsch, *Journ. Soc. Chem. Ind.* 1896, 14.

cholesterol are formed. This product is, however, not obtained if the cholesterol be heated with normal or 1½ normal potash in a sealed tube to 112°-115° C.[1]

Colour Reactions of Cholesterol (cp. Lewkowitsch, *Journ. Soc. Chem. Ind.* 1892, 144).

The following reactions have been recommended by *Schulze*:—

1. If a minute quantity of cholesterol be carefully heated with a drop of concentrated nitric acid to dryness on a crucible cover, a yellow stain is obtained; on pouring a little ammonia on it, a yellowish-red tint is produced.

2. If a little cholesterol be triturated on a crucible cover with one drop of a mixture, consisting of three measures of concentrated hydrochloric acid and one measure of a 10 per cent solution of ferric chloride, a violet-red colouration is produced, changing to blue on evaporating to dryness. It must, however, be remembered that oil of turpentine, camphor, and other substances behave in the same manner.

A very delicate and characteristic reaction has been described by *Hager*, and slightly modified by *Salkowski*. A few centigrammes of cholesterol are dissolved in 2 c.c. of chloroform, an equal volume of concentrated sulphuric acid is added, and the mixture shaken. The chloroformic solution immediately becomes coloured blood-red, afterwards cherry-red and purple; the last tint remains for several days. The sulphuric acid layer under the chloroform shows a strong green fluorescence.[2] On pouring a few drops of the purple chloroform layer into a porcelain basin, the red colour changes rapidly to blue, green, and finally to yellow. On diluting the purple chloroformic solution with more chloroform, it becomes nearly colourless or acquires an intense blue colour; if it now be shaken again with the sulphuric acid layer, the former colouration reappears. These changes of colour are due to traces of water in the chloroform.[3]

If on shaking a chloroformic solution of cholesterol, prepared from fats, with concentrated sulphuric acid, the blue colouration is noticed at once, the presence of so-called "lipochromes" is indicated, which have been shown to occur in cod liver oil, the fat of the yolk of eggs, palm oil, and in small quantities in cow butter. But even in these cases the red colouration soon appears.

Liebermann's "cholestol" reaction is very characteristic, and is shown by the minutest quantities of cholesterol. A solution of cholesterol in acetic anhydride gives a violet-pink colouration[4] on adding concentrated sulphuric acid, drop by drop. Sharper still is the modified form of this test as proposed by *Burchard*:—Dissolve a little cholesterol in 2 c.c. of chloroform, add 20 drops of acetic anhydride, and one drop of concentrated sulphuric acid. Unfor-

[1] Darmstaedter and Lifschütz, *Berichte*, 1898, 1126.

[2] In the case of wool-fat cholesterol this green fluorescence is, in my opinion, due to presence of isocholesterol.

[3] According to Herbig (*Dingl. Polyt. Journ.* 1897 (303) 191) cholesteryl palmitate and cholesteryl cerotate give the same colour reaction.

[4] Wool-fat cholesterol does not show the violet-pink given by gall-stone cholesterol, but becomes red at once.

tunately rosin acids (colophony) and other substances give the same or very similar reactions.

Isocholesterol, $C_{26}H_{44}O$ ($C_{27}H_{44}O$?)

This alcohol is isomeric with cholesterol, and resembles it in many respects. It occurs together with cholesterol in wool fat. Isocholesterol isolated from its benzoate (*Schulze*) crystallises from ether in fine needles, melting at 137°-138° C. It dissolves sparingly in cold, but rapidly in boiling alcohol, from which, on cooling, it separates in a jelly-like mass. It is readily soluble in ether and in petroleum ether.

Isocholesterol is optically active; in contradistinction to cholesterol it is dextro-rotatory. $[\alpha]_D = +60°$ in ethereal solution.

Isocholesteryl acetate, $C_{26}H_{43}O \cdot C_2H_3O$, has been obtained as an uncrystallisable mass.

Isocholesteryl benzoate, $C_{26}H_{43}O \cdot C_7H_5O$, is a crystalline powder, consisting of very fine needles melting at 194°-195° C. It dissolves sparingly in alcohol, more easily in hot acetone and in ether.

Colour Reactions of Isocholesterol.—Isocholesterol gives the same reaction as cholesterol with nitric acid and ammonia. On adding one drop of concentrated sulphuric acid to a solution of isocholesterol in acetic anhydride, a yellow and afterwards a reddish-yellow colouration is obtained, showing at the same time a green fluorescence. The same reaction becomes more distinct on employing *Liebermann's* "cholestol" test in the form proposed by *Burchard* (see above).

In a mixture of cholesterol and isocholesterol the colour reaction of the latter seems to prevail and to mask the violet-pink colouration due to cholesterol.

Phytosterol, $C_{26}H_{44}O$ ($C_{27}H_{44}O$?)

Phytosterol, the "cholesterol of plants," is widely disseminated in the vegetable kingdom and occurs in all seeds and fruits. In the preparation of vegetable oils and fats small quantities pass into the latter, forming a very characteristic concomitant thereof. The proportion of phytosterol in vegetable oils and fats is somewhat larger than that of cholesterol in animal oils and fats.

Phytosterol in many respects resembles cholesterol; it differs, however, from it in its crystalline form and melting point. The crystals of cholesterol deposited from its hot alcoholic solution appear as a magma of laminæ, which are discerned, under a microscope, as very thin plates, showing often re-entering angles; these plates are apparently rhombic, but belong most likely to the triclinic system (*Bömer*). Phytosterol, however, crystallises in solid needles, grouped in tufts; under the microscope there are discerned long, solid needles arranged in star- or bunch-like groups; these crystals belong most likely to the monoclinic system. The crystals have the composition expressed by the formula $C_{26}H_{44}O + H_2O$; they melt at 137°-138° C.

(*Bömer*), 138°-143·8° (corr.) according to the purity of the preparations, whereas the melting point of cholesterol is 148·4°-150·8° C. From a mixture of cholesterol and phytosterol the components do not crystallise separately; if the latter predominates or is present in approximately the same proportion as cholesterol, the crystals cannot be discerned from those of phytosterol. If cholesterol predominates needles of a quite different form separate (*Bömer*). Crystals obtained from (1) a mixture of 3 parts phytosterol and 1 part of cholesterol melt between 135·6°-136·0° C.; (2) equal parts of phytosterol and cholesterol melt between 140·0°-141·5° C.; and (3) 1 part of phytosterol and 3 parts of cholesterol melt between 143·7°-145·0° C. The crystalline forms of cholesterol, phytosterol, and mixtures of the two alcohols are shown on chap. ix. p. 370. Phytosterol is lævorotatory; $[\alpha]_D = -34{\cdot}2$. Phytosterol is easily soluble in ether, less so in petroleum ether; 100 c.c. of the latter (specific gravity 0·7522, boiling point 35°-85° C.) dissolve only 2·792 grms. (*Bömer*).

A chloroformic solution of phytosterol gives the same reaction with sulphuric acid as the corresponding solution of cholesterol, but with the slight difference that the colouration obtained with phytosterol passes after a few days into a bluish-red, whereas the cholesterol solution becomes more of a cherry-red.

It has been pointed out already that animal oils and fats can be distinguished from vegetable oils and fats by the presence of cholesterol in the former, and phytosterol in the latter; hence the isolation of cholesterol and phytosterol has become an important operation in fat analysis. With a view to working out a reliable method, *Bömer*[1] instituted an exhaustive investigation of the esters of cholesterol and phytosterol, his object being to detect the most characteristic derivatives, leading to the ready identification of the original alcohol.

Therefore, the properties of the esters have acquired sufficient importance to deserve here extended notice.

Esters of Cholesterol

Cholesteryl formate, $C_{26}H_{43}O.CHO$, crystallises in long, fine needles, melting at 96·8° C. (corr.).

Cholesteryl acetate, $C_{26}H_{43}O.C_2H_3O$, is prepared by boiling cholesterol with one and a half times its quantity of acetic anhydride in a flask connected with an inverted condenser. This reaction also may be used for the quantitative determination of cholesterol.[2] Cholesteryl acetate crystallises in small needles, nearly insoluble in cold, and sparingly soluble in boiling alcohol. The crystals melt at 114° C.; 114·3°-114·8° C. (corr. *Bömer*).

Cholesteryl propionate, $C_{26}H_{43}O.C_3H_5O$, crystallises in the form of very fine needles; it melts at 98° C. (*Obermüller*), 96·8° C. (corr. *Bömer*).

[1] *Zeit. f. Unters. d. Nahr. und Genussm.* 1898, 21, 81; 1901, 878.
[2] Lewkowitsch, *Journ. Soc. Chem. Ind.* 1896, 14.

Cholesteryl (normal) *butyrate*, $C_{26}H_{43}O . C_4H_7O$, crystallises in the form of short, fine needles, it melts at 95°-96·8° C. (corr. *Bömer*).

Cholesteryl benzoate, $C_{26}H_{43}O . C_7H_5O$, is formed by heating cholesterol with benzoic anhydride in a sealed tube to a temperature of 200° C. It is nearly insoluble in boiling alcohol, and crystallises from ether in rectangular plates, melting at 150°-151° C. (*Schulze*), 145·5° C. (*Obermüller*), 148·4° C. (corr. *Bömer*).

Esters of Phytosterol

Phytosteryl formate, $C_{26}H_{43}O . CHO$. The crystals closely resemble those of phytosterol itself. The ester melts at 105·5°-114·3° C. (corr.) according to the purity of the various preparations of phytosterol obtained from the different oils.

Phytosteryl acetate, $C_{26}H_{43}O . C_2H_3O$, crystallises from a concentrated solution in bunches of very fine needles; from a very dilute solution, plates resembling phytosterol itself were very frequently obtained. The melting point of the acetate is 125·6°-137° C. (corr. *Bömer*), according to the purity of the preparations obtained from the different oils.

Phytosteryl propionate, $C_{26}H_{43}O . C_3H_5O$. The crystals are mostly obtained as very fine needles; occasionally they formed large plates very similar to those which phytosterol itself exhibits. The melting point varies from 106° to 117·3° C., according to the purity of the preparations obtained from the various oils.

Phytosteryl (normal) *butyrate*, $C_{26}H_{43}O . C_4H_7O$, crystallises in forms very similar to those of phytosterol itself. The crystals melt at 68·5°-90·6° C. (corr.), according to the purity of the preparations obtained.

Phytosteryl benzoate, $C_{26}H_{43}O . C_7H_5O$, crystallises in rectangular plates very similar to those of cholesteryl benzoate. Preparations obtained from cotton seed oil, and sesamé oil phytosterol, melted at 145·3°-148·4° C. (corr.)

SITOSTEROL, $C_{27}H_{44}O + H_2O$

Sitosterol[1] is found in the "unsaponifiable matter" of the oils from wheat and other germs of the gramineæ. Hence, the "cholesterol" stated by *Hoppe-Seyler* and *Hopkins* to occur in maize oil is most likely sitosterol.[2] It crystallises in white laminæ of silky lustre, simulating the appearance of gall cholesterol. From dilute alcohol, sitosterol crystallises with one molecule of water; it crystallises from ether in anhydrous needles. Sitosterol melts at 137·5° C. It is easily soluble in ether, chloroform, benzene, carbon bisulphide, and hot alcohol, but sparingly soluble in cold alcohol. Sitosterol is lævo-rotatory; $[\alpha]_D = -26·71$. In the *Liebermann-Burchard*

[1] *Monatsh. f. Chem.* 1897 (18), 561.
[2] A. H. Gill and C. G. Tufts, *Journ. Amer. Chem. Soc.* 1903, 25, 251.

cholestol test, as also in the *Salkowski* reaction, sitosterol behaves like cholesterol.

Sitosteryl acetate, $C_{27}H_{43}O \cdot C_2H_3O$, melts at 127·5° C.

Sitosteryl propionate, $C_{27}H_{43}O \cdot C_3H_5O$, crystallises in white laminæ resembling cholesterol; the crystals melt at 108·5° C.

Sitosteryl benzoate, $C_{27}H_{43}O \cdot C_7H_5O$, melts at 145°-145·5° C.

The chemistry of the cholesterol and phytosterol group has not yet been fully investigated. A number of alcohols having the same composition have been described under various names such as caulosterol,[1] ergosterol, hydrocaroton, etc. Since *Bömer* obtained phytosterols varying in melting point from different oils, and since the small quantities obtained are very difficult to purify, and hence must necessarily differ in their melting points, it is very likely that some of these alcohols which have been described as separate individuals, such as peas-alcohol, beans-alcohol, etc., are very likely identical with phytosterol.

The most prominent characteristics of a number of these various alcohols have been recorded by *Burian*.[2]

[1] Frankforter and Harding, *Journ. Soc. Chem. Ind.* 1899, 1031.
[2] *Monatsh. f. Chem.* 1897 (18), 551.

CHAPTER IV

PREPARATION OF THE FATTY MATTER FOR EXAMINATION —PRELIMINARY TESTS

THE production, refining, bleaching, etc., of the raw materials used in the oil and fat industries will be discussed in the second volume of this work. In this section I shall deal with the fatty materials as they reach the works' yard or the laboratory. Preparatory to the analytical examination by physical and chemical methods, the fatty matter must be freed from foreign substances.

Sampling

In sampling a cask of fat one must be careful to obtain a sample which shall actually represent the bulk. This can easily be done with liquid fats, and all that is necessary is to well stir into the bulk of the oil any separated "stearine" (as in the case of cotton seed oil). In the case, however, of solid fats care must be exercised, or grave errors may be committed.

The following reliable method of sampling tallow and other solid fats is the one used at seaports and in works. By means of an auger a cylindrical sample of fat, at least eight inches long and one inch thick, is taken from each cask, or a convenient number of casks, and each sample is labelled with the number and marks of the cask, the gross weight and tare of each cask being also noted. The several samples are mixed by the chemist in quantities corresponding to the net weight of their respective casks, and the mass thus obtained is melted on the water-bath in a dish, at a temperature not exceeding 60° C., with constant stirring. As soon as the fat is melted, the dish is removed from the water-bath and the mass stirred vigorously in order to prevent water and impurities from settling down to the bottom of the dish.

The first operation in the examination of fats is the estimation of water and of substances of a non-fatty nature, which can be readily separated from the fat. It should be borne in mind, that a number of substances, such as rosin, paraffin wax, paraffin oils, tar oils, and rosin oils, may be retained by the fat in intimate intermixture with

it. These substances, if we except rosin, are comprised under the term "unsaponifiable matter." Their determination, including that of rosin, is carried out when the examination of the dry and preliminarily purified fat is reached.

Estimation of Water

About 5 grms. of the fat are accurately weighed in a small beaker or flask containing a thin glass rod, and dried at 100° to 110° C. until the weight remains constant, or, at any rate, the loss in one hour does not exceed 1 or 2 mgrms. (cp. p. 264). The drying should not be pushed beyond a point when approximately concordant results have been obtained, which as a rule will be reached within a few hours. Otherwise slight loss may be caused by volatilisation of lower fatty acids (either contained originally in the substance or formed at the higher temperature), or an increase of weight may take place owing to absorption of oxygen. It is quite possible, of course, that both volatilisation and consequent decrease of weight on the one hand, and oxidation and consequent increase of weight on the other hand, may occur simultaneously, these two sources of error to some extent balancing one another (cp. also p. 263).

Whilst drying, the fat is conveniently stirred from time to time, as water will collect below the fat, and only slowly evaporates through it. This method will be found to answer in the case of solid and not easily oxidisable fats. In the case of drying oils, if great accuracy is required, it is advisable to dry in a current of carbonic anhydride or coal gas or hydrogen. The oil is then best weighed in a flask closed by a cork perforated with two holes, through one of which passes a straight tube to the bottom of the flask, whilst the other is fitted with a bent tube ending with the cork. A calcium chloride tube is then attached to the straight tube, the bent tube is connected with the filter pump, and a current of gas is drawn through the oil at 100° C.[1]

For the determination of water in cow butter, *Henzold* recommends especially the following method: Weigh off 20 grms. of freshly heated pumice stone, cooled under a desiccator, in a shallow dish, add 10 to 12 grms. of the fat, and heat to 100° C. for two hours, stirring occasionally with a glass rod which has been tared with the dish.

In case caustic potash, or potash soap, or lime soap have been fraudulently added to tallow, etc. (in order to facilitate the incorporation of water), the fat cannot be freed from the last traces of water by drying at 100° C. Bone fats normally retain lime soaps which do not readily part with the contained moisture even at 130° C. The safest plan in these cases is to determine the amount of fatty matter, impurities, and of potash or lime separately, and to find the percentage of water by difference (cp. "Bone Fat," chap. xiv.).

[1] Cp. *Journ. Soc. Chem. Ind.* 1886, 508 (Illustration).

Determination of Foreign Substances

To determine solid substances, such as remnants of vegetable or animal tissue, dirt, or fraudulent admixtures, 10-20 grms. of the dried[1] fat are extracted in a flask by shaking with one of the following solvents: petroleum ether, chloroform, carbon tetrachloride, ether, or benzene. The solution is then poured through a tared filter and the residue washed on the filter with the same solvent, until a few drops of the filtrate, evaporated on paper, no longer leave a grease-spot. The filter with its contents is then dried at 100° C. and weighed. The dried residue may be incinerated and weighed again, when the difference will give the amount of organic matter. If the amount of ash is large (salt, chalk, clay, or lime from fraudulently added lime soap), further examination of these foreign matters may be required.

Of the foregoing solvents, petroleum ether will be found the most convenient, inasmuch as it dissolves smaller quantities of resinous bodies than any of the other solvents mentioned. Therefore, if there be no reason against the use of petroleum ether—*e.g.* in the case of castor seed—this solvent should be employed; all the more so, as it can easily be obtained in a state of purity and free from acid; besides, it need not be dried beforehand. It should, however, be rectified carefully by means of a fractionating column, and all portions boiling above 80° C. should be discarded. If necessary, it should be purified by shaking with a little concentrated sulphuric acid; after separation from the dark acid layer the petroleum ether must be washed with water until entirely free from acid.

In the case of bone fats it has been shown by *Shukoff* and *Schestakoff*[2] that the choice of the solvent is not immaterial, as carbon bisulphide indicates less insoluble matter than petroleum ether; the former solvent also extracts more lime soap in the hot than in the cold. Thus a sample of bone fat treated with hot carbon bisulphide gave 1·1 per cent of insoluble matter when filtered rapidly, whereas after cooling the solvent 6·5 per cent were obtained.

If a considerable quantity of organic matter has remained on the filter, the residue should be tested for metallic soaps (lime soaps, aluminium soaps, etc.) and for starch. On treating with mineral acids, the soaps will be decomposed with liberation of fatty acids which remain on the filter, whilst the metals will pass into the aqueous solution.

Starch can be detected in the organic residue by means of the blue colouration it gives with iodine solution, and its presence may be confirmed by microscopical examination. It is important to note that on dissolving a fat in petroleum ether, etc., starchy matter is liable to retain some fat. Hence the amount of starch found does not correspond exactly to the weight of the dried residue. *König* recommends, therefore, especially in butter analysis, to wash the residue, after exhaustion with ether, with cold water, in order to remove any water-soluble substances. The residue is made soluble

[1] With regard to Bone Fats, cp. chap. xiv.

[2] *Journ. Soc. Chem. Ind.* 1898, 805. *Chem. Revue*, 1898, 6.

by boiling with water, and finally converted into glucose by heating with hydrochloric acid. The glucose may be estimated by means of *Fehling's* solution.

Substances **soluble in water** (some of them, *e.g.* common salt, may be found on the filter) are removed from the fat by shaking a large quantity, say 50-100 grms., with warm water, so as to liquefy the fat. The mixture is allowed to stand in a warm place until it has separated completely into two layers. Should the separation not be complete after a short time, or should part of the fat form an emulsion with the aqueous layer, addition of a little ether will be found effective in causing separation. The aqueous liquid is then removed by means of a separating funnel and examined. Any existing traces of sulphuric acid (left in the oil from refining operations) will be found in this aqueous layer, and may be estimated by titration with standard alkali, using methylorange as indicator. Other substances present may be determined in the residue left on evaporation.

Ethereal oils contained in the fats, as in nutmeg butter, are best determined by distillation in a current of steam. On weighing the remaining dried fat the quantity of essential oils will be found by difference. The distillate may be shaken out with ether, and the ether residue further examined.

Determination of Fat in the Sample

The determination of true fat in a sample may be conveniently combined with the estimation of foreign substances, as already described, by collecting the filtrate in a tared flask, evaporating the solvent, and weighing the dried residue.

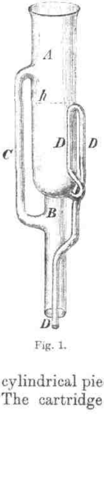


Fig. 1.

If mucilaginous, or starchy, or other solid substances are intermixed with the fat, the following process will be found more convenient and also more reliable. The sample is intimately mixed with 4-6 times its weight of sand or finely powdered gypsum (previously washed and heated), and the mixture dried at 100° C. It is then transferred to an automatic exhausting extractor.

The most convenient apparatus for extraction of fat is the one devised by *Soxhlet* (*Szombathy*) (Fig. 1). A modification of this apparatus, which is preferred by many as being less liable to break, is shown in Fig. 2.

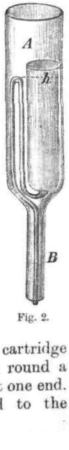


Fig. 2.

The substance to be extracted is put into a cartridge of filter paper, easily prepared by rolling it round a cylindrical piece of wood of suitable size, and folding it up at one end. The cartridge is filled with the substance and transferred to the

extractor A. Care must be taken that the syphon tube is not stopped up by the paper case; nor should the cartridge be filled up to the top, lest some particles of the substance be washed over by the solvent and be carried away. To be quite safe, it will be found convenient to place a plug of (extracted) cotton-wool on the top of the substance, or to close the top by folding the paper. The tube B is then fitted by means of a cork to a flask holding 100-150 c.c., and containing about 50 c.c. of the solvent (petroleum ether, ether, chloroform, etc.) Another portion of the solvent is carefully poured on to the substance in B, until it commences to run off through the syphon D. Finally an inverted condenser is adapted to A, and the whole apparatus placed on a water-bath. As the solvent boils, the vapours pass through B and C into the condenser, and fall condensed on the substance in the paper case. When the liquid has reached the level *h*, the solution syphons off automatically through D, and A is emptied completely. The solvent is again evaporated and recondensed, and serves again for extracting, and so on. In this way the vessel A may easily be filled and emptied twenty to thirty times within an hour.

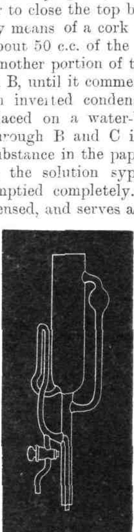


Fig. 3.

In using the form of *Soxhlet's* extractor described above, there is always some doubt as to the exact time when the exhaustion is completed, and, as a rule, the operation lasts much longer than necessary, involving both loss of time and of solvent. To avoid this *Lewkowitsch*[1] has a tap fitted on to the syphon tube, so that some of the solvent may be withdrawn at any time, and the progress of extraction ascertained (Fig. 3).

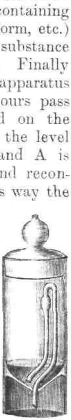


Fig. 4.

If the substance to be exhausted has been collected on a filter, the simplest plan is to fold the filter up and place it at once in the extractor.

Frühling[2] proposed a modified form of the Soxhlet extractor which admits of convenient handling on weighing before and after the extraction. The essential part of the apparatus, serving for the reception of the sample, is shown in Fig. 4. It has the form of an ordinary filter-weighing bottle, differing only from it in that the bottom has a funnel-like shape. It is provided with a syphon, the longer limb of which passes through the bottom, where it is cut off aslant. The sides of **A** are continued beyond the protruding limb of the syphon, so as to allow of its standing in an upright position on the pan of a balance, and at the same time serving to protect the tube from breakage. The shorter limb of the syphon reaches to the bottom of the bottle, and is provided with a bulb in its upper part,

[1] *Journ. Chem. Soc.* 1889, 360. [2] *Journ. Soc. Chem. Ind.* 1889, 568.

which serves to sever the column of the solvent when the bottle is taken out of the tube B (Fig. 5). This tube is the ordinary form of the Soxhlet extractor without its syphon tube, and serves for the reception of A. The upper part of B may be fitted with a carefully-ground stopper, having tube C attached to it. The whole arrangement and application of the apparatus will be readily understood from a glance at the annexed figures.

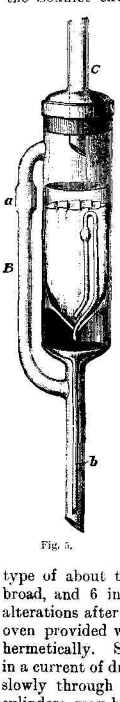


Fig. 5.

For the extraction of substances at the boiling point of the solvent, *F. K. Stock* recommended a suitably modified extractor.[1]

The number of modifications and improvements of *Soxhlet's* ingenious apparatus is almost legion. As the above-described forms will be found suitable for most purposes, the reader must be referred for further information to the pages of the *Journal of the Society of Chemical Industry*, where a complete record of all proposed forms will be found.

When the extraction is completed the flask containing the solution is detached from the extractor, the solvent distilled off on the water-bath, and the fat dried in an air-bath at a temperature not exceeding 100°-110° C. until the weight remains fairly constant (cp. p. 264).

The apparatus described will also be found useful for the estimation of fat contained in oleaginous seeds, oil-cakes, etc. Previous to the extraction, these substances must be disintegrated to a fine powder, and, if required, dried at a suitable temperature (cp. chap. xiii.).

The drying and filtering of the fat is best carried out in a spacious drying oven provided with a thermostat (thermo-regulator).

The drying oven may be one of the customary type of about the following dimensions: 10 inches high, 10 inches broad, and 6 inches deep. An apparatus I had made with slight alterations after *Sidersky's*[2] design, consists of a jacketed cylindrical oven provided with a door having a thick glass plate and closing hermetically. Suitable taps allow the drying to proceed *in vacuo* or in a current of dried air or of an indifferent gas, which can be aspirated slowly through the drying chamber. The space between the two cylinders may be filled with water or any other suitable liquid, and thus the desired temperature may be kept constant without attention for any length of time.

Reichert's improved form of thermo-regulator is represented by Fig. 6. It consists of a capillary tube enlarged at the bottom to a bulb *c*,—in short, of a thermometer, the top part of which is widened out as shown. The capillary branch tube is supplied with a screw S,

[1] *Journ. Soc. Chem. Ind.* 1897, 107. [2] *Ibid.* 1890, 967.

by means of which the level of the mercury may be adjusted at will. The gas-supply tube A is carefully ground into the upper part of the thermometer tube, and extends down to the joint of the stem. A has an opening at the bottom, and is also perforated with a very small hole at *a*. The gas entering A leaves the regulator at B. The thermostat is fixed along with an ordinary thermometer by means of a cork perforated with two holes into a nozzle of the drying oven; A is then connected with the gas supply, and B with the gas burner. The tube A must be adjusted in such a way that communication with B is established through *a*, whilst S has been screwed out of the tube sufficiently to allow the mercury to fall below the tapered part. The oven is then heated, and at the moment the desired temperature has been reached, S is screwed into the tube until the column of mercury just reaches the tube A. The exact moment is easily observed by the flame of the burner becoming smaller. Gas is then supplied to the burner through *a* only, until in consequence of the falling of the temperature in the oven the mercury falls, thus allowing an additional supply of gas to flow through the lower end of A, which had been closed before by the mercury. With a rise of temperature the mercury expands, and again closes the lower opening of A, thus causing the temperature to fall, and so on. It is thus possible to keep the temperature nearly constant within very narrow limits. In the case of the flame of the burner being too high for the desired temperature, even when gas passes through *a* only, the gas supply must be diminished by turning the tube A a little, thus partially closing the opening *a*.

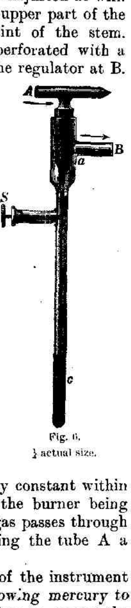


Fig. 6.
½ actual size.

The screw S is usually cemented by the maker of the instrument with sealing-wax, which, however, easily melts, allowing mercury to ooze through the cork; care should therefore be taken to protect the wax from becoming overheated.[1]

Another objection to *Reichert's* thermostat has been pointed out by *J. W. James*,[2] namely, that after short use,—a few days or weeks, depending on the purity of the gas,—the upper surface of the mercury becomes coated with a black powder (mercuric sulphide) which before long impairs the delicacy of the regulator. It becomes then necessary to take the apparatus to pieces for cleaning. *James* has therefore designed a thermostat, making use of *Reichert's* principle, but avoiding the objectionable passing of the gas over the surface of the mercury. For the drawing and instructions for use the original paper should be consulted. Another new thermostat, made

[1] The principle underlying Reichert's thermo-regulator, but avoiding the last mentioned drawback, has been employed by *Berlemont*, cp. *Journ. Soc. Chem. Ind.* 1895, 821.
[2] *Journ. Soc. Chem. Ind.* 1893, 225.

entirely of metal and not containing mercury, has been described by *Porges*.[1]

In a laboratory provided with steam it is most convenient to connect the jacketed drying oven with the steam supply; a thermostat can then be dispensed with.

If it is merely a question of freeing a sample of fat from water and gross impurities for subsequent examination, the fat is best melted in a dish in the water-bath and kept on it until the water and dirt have settled out. The clear fat is then poured off through a dried filter, which will absorb the small quantities of moisture dissolved in the fat.

Detection and Determination of Inorganic Substances in the Fatty Matter

Oils and fats have the property of dissolving small quantities of water-soluble as well as metallic soaps. In "boiled" oils metallic soaps are present as a normal constituent. The presence of metals is readily ascertained by burning off a few grams of fat in a crucible; if metal be present, a residue is obtained.

The following bases may have to be tested for: sodium and potassium hydrates, lime, alumina, and the oxides of lead, copper, and zinc.

In the presence of the *alkali metals* the residue will dissolve in water, and show an alkaline reaction to litmus paper. Sodium and potassium salts are identified by applying the methods used in the analysis of soaps (chap. xv.).

If lime be suspected, the ash is treated with dilute hydrochloric acid. After filtering, the filtrate is tested with ammonium oxalate and ammonia. A white precipitate will prove the presence of lime.

For the quantitative estimation of lime proceed as above, but allow the precipitated calcium oxalate to stand in a moderately warm place for twelve hours, filter and dry the residue, and heat over the blowpipe until the weight of the calcium oxide remains constant.

The separation of other metals from an oil or fat is best effected by warming the sample on the water-bath with very dilute nitric acid in a flask; they then pass into the acid liquid. Or a somewhat large quantity of the fat may be incinerated in a platinum dish (if lead be suspected, in a porcelain crucible), the resulting ash dissolved in a few drops of nitric acid, and the solution diluted with water. A less convenient process is to dissolve the fat under examination in ether, and to shake out with acidulated water.

Part of the acid solution obtained by any of the preceding methods is tested with sulphuretted hydrogen, when the presence of a heavy metal will be indicated by the appearance of a black or brown precipitate or colouration.

[1] *Zeitsch. f. analyt. Chemie*, 1893, 212.

Other portions of the solution are tested (1) with potassium ferrocyanide (brown precipitate), and with ammonia (blue colouration) for *copper*; (2) with sulphuric acid (white precipitate), and with potassium chromate (yellow precipitate, soluble in potash) for *lead*. For the detection and estimation of *iron* see below. *Zinc* and *alumina* are tested for by the well-known methods of qualitative analysis.

Copper oxide is sometimes mixed with oils in order to impart to them a green colour. Rancid fats (such as lard), when kept in copper or in lead-glazed vessels, may easily dissolve some **copper or lead.** The detection of these two metals in edible oils and fats deserves, therefore, special attention.

Quantitative Determination of Copper

Weigh off accurately 10 to 20 grms. of the fat under examination in a platinum dish and incinerate. Dissolve the ash in a few drops of nitric acid, dilute with water, and filter into a beaker. Heat the solution nearly to the boiling point, add pure caustic soda or potash, and heat again for a few minutes. Filter off the black precipitate of copper oxide, dry, ignite, and weigh.

Another method is to thoroughly stir the warmed fat with hydrochloric acid, and pour the acid liquid through a filter; the fat is then washed several times with water; and the washings added to the main portion. Next the solution is heated whilst a current of sulphuretted hydrogen is passed through. The precipitated cupric sulphide is filtered off, washed with water containing sulphuretted hydrogen, dried, mixed with sulphur, and heated in a porcelain crucible in a current of hydrogen. The copper is thus converted into cuprous sulphide, Cu_2S.

Quantitative Determination of Lead

(1) The lead is brought into solution as lead nitrate by one of the methods detailed above. Dilute sulphuric acid is then added, and the solution warmed on the water-bath until all the nitric acid has evaporated off. The remaining liquid is mixed with a little water and twice the volume of alcohol. After allowing to stand for a few hours the precipitate is filtered off, washed with dilute alcohol, dried, and ignited. The filter, of course, must be incinerated separately. The resulting lead sulphate is calculated to *lead oxide* or *lead*.

(2) A more rapid, though less accurate method, is the following:—Burn off several grms. of the fat in a tared porcelain crucible. The residue, consisting of a mixture of metallic lead and lead oxide, is weighed first, and then treated with warm acetic acid to dissolve the lead oxide. The metallic lead is washed by decantation, and the crucible dried and weighed again, whereby the amount of metallic lead is found. The difference between the two last weights corresponds

to the amount of lead oxide; it is calculated to lead, and the quantity added to that found for the metallic lead.

(3) Shake the ethereal solution of the fat or oil with dilute sulphuric acid, filter, ignite the precipitate, and weigh as lead sulphate.[1]

Detection and Estimation of Iron

Oils used for dyeing purposes and for currying leather should be free from iron. Alizarin oil (which usually contains from 15 to 20 per cent of free fatty acids), if kept in iron vessels, is especially liable to be contaminated, and the examination of Turkey-red oils for iron is therefore important.

Emde[2] describes the following convenient method. The oil is shaken in a graduated cylinder with water acidulated with sulphuric acid. A few drops of potassium ferrocyanide are added, and the whole shaken up with a little ether. The oil dissolves in the ether, and forms a sharply-defined layer on the water. In the presence of iron, a more or less dense layer of Prussian blue, containing all the iron, will appear on the border line between the two liquids. Comparative tests with the same quantities of iron-free oil, water, acid, and potassium ferrocyanide admit of a rough estimation of the quantity of iron.

For accurate estimation it is of course necessary to precipitate the iron as hydrated ferric oxide and weigh it as ferric oxide.[1]

Other inorganic substances which may occur as impurities are sulphur, phosphorus, and chlorine. They are detected and estimated as follows :—

QUALITATIVE TEST FOR SULPHUR

Oils which have been extracted by carbon bisulphide may retain small quantities of sulphur.

Sulphur is detected by saponifying the sample with caustic soda or caustic potash, when sodium or potassium sulphide is formed. On adding to the soap solution an alkaline lead solution, a black or brown precipitate will be obtained in the presence of sulphur.

A rapid method to detect sulphur is to immerse a bright silver coin into the boiling oil. In presence of sulphur the coin will become brown or black.

Sulphuric acid or sulphonated oils (or their fatty acids) cannot be detected by the preceding methods. On washing the sample with water any sulphuric acid present will pass into the aqueous layer, and can be detected by barium chloride. Sulphonated products obtained by prolonged treatment of the oil with sulphuric acid (see Turkey-red Oil), must be decomposed first, either by boiling with hydrochloric acid or by fusing with caustic potash and potassium nitrate.

[1] Fresenius and Schattenfroh, *Journ. Soc. Chem. Ind.* 1895, 895.

[2] *Journ. Soc. Chem. Ind.* 1888, 591.

QUANTITATIVE DETERMINATION OF SULPHUR

(*a*) *Liebig's Method.*—Weigh off carefully a somewhat large quantity of the sample, and saponify it in a silver dish with alcoholic potash; boil down until the mass becomes syrupy, allow to cool, add a few sticks of pure caustic potash and some potassium nitrate—about one-eighth of the weight of the potash used—and finally a few drops of water. Heat the mass carefully, with constant stirring—using a silver stirrer—and raise the heat gradually until the mass is fused and has become perfectly white. Then allow to cool, dissolve in water, and transfer to a large beaker, in which the sulphuric acid formed is precipitated in the usual way with barium chloride. In very accurate work it is preferable to boil out the heated barium sulphate with dilute hydrochloric acid and to weigh again.

(*b*) *Allen's Method.*—*Allen*[1] proposes for the determination of the sulphur in oils, an apparatus similar to that used for the estimation of sulphur in coal gas (Fig. 7). Five grams of the oil are mixed with 45 grms. of purified methylated spirit, and burnt in the lamp A fitted into the wider end of a curved adapter. *e* contains solid ammonium carbonate. The gases pass through C into the condenser D filled with wetted glass balls. The lower end of D is furnished with a glass stop-cock *h* for drawing off the condensed liquid. A second condenser G is attached to D to condense the vapours escaping from D. The upper tubulure of G is connected with an aspirator to produce a slight draught. The flame should be a small one, and should be surrounded by wire gauze to prevent overheating. The liquid drawn from the condensers contains the sulphur as sulphite and sulphate, which are estimated by well-known methods.

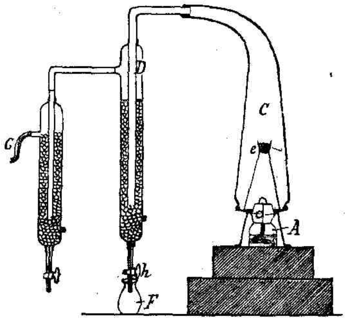


Fig. 7.

Similar contrivances have been described by *Mabery*,[2] *Heusler*,[3] *Engler*,[4] and *Kissling*.[5]

[1] *Analyst*, 1888, 43. Cp. the Apparatus adopted by the Metropolitan Gas Referees.
[2] *Journ. Soc. Chem. Ind.* 1895, 197.
[3] *Ibid.* 1895, 828. [4] *Ibid.* 1896, 383 [5] *Ibid.* 1896, 384.

Estimation of Phosphorus

In order to determine phosphorus, as in fats containing lecithin, the sample is saponified with alcoholic potash; the alcohol is evaporated off, and the diluted soap solution shaken out with ether, in order to remove any cholesterol present. The soap solution is then decomposed by a mineral acid, and the fatty acids separated from the acid liquid. The latter contains all the phosphorus as glycerol-phosphoric acid, $C_3H_5(OH)_2PO_4H_2$. It is boiled down to dryness and the residue fused with potassium hydrate and potassium nitrate. The melt is then dissolved in water, and the phosphoric acid precipitated by magnesia mixture and weighed as pyrophosphate. On multiplying the P_2O_5 found by 11·366, the amount of *lecithin*, $C_{44}H_{90}NPO_9$, will be obtained. (On saponification lecithin yields choline, glycerol-phosphoric acid, and fatty acids. The latter are stated by *Cousin*[1] to consist, in the case of egg-lecithin, of 24 per cent linolic, 28·5 per cent palmitic, and 14·2 per cent of stearic acids.)

The following table contains the proportions of lecithin found in oils and fats:—

Oil or Fat.	Phosphorus.	Phosphorus. Calculated to Lecithin.	Observer.
	Per cent.	Per cent.	
Linseed	...	0·33	Jaeckle
Poppy seed	...	0	,,
Maize	...	1·49	Hopkins
Sorghum	...	0·23	Andrejew
Cotton seed	...	0·0025-0·006	Jaeckle
Sesamé	...	0·005	,,
Wheat	0·25	6·5 (?)	Töpler
Peas	1·17	30·5 (?)	,,
Rape	...	0·11	Jaeckle
Almond	...	0·03	,,
Arachis	..	traces	,,
Egg	...	0·2	Kitt
Cod liver	...	0·005	Jaeckle
Cacao butter	...	0·11	,,
Cocoa nut	...	0·01	,,
Hare	...	0·03	,,
Goose	...	traces	,,
Lard	...	0·022-0·051	,,
,, American	...	0·006	,,
Human	...	0·073-0·084	,,
Beef tallow	...	0·033-0·073	,,
Mutton ,,	...	0·01	,,
Butter	...	0·000-0·014	,,

It should, however, be noted that it is not permissible, without further investigation, to calculate the phosphorus found to lecithin. Thus a considerable amount of the phosphorus in linseed oil is present as calcium or magnesium phosphate.

[1] *Journ. Pharm. Chim.* 1903, 102.

In order to determine the phosphorus in phosphorised oils, such as in phosphorised almond and cod liver oils, 5-10 grms. of the sample are dissolved in 100-200 c.c. of acetone, and the phosphorus precipitated as silver phosphide by adding a 10 per cent silver nitrate solution. The precipitate is then filtered off and oxidised with nitric acid. The silver is precipitated with hydrochloric acid, and the phosphoric acid determined in the filtrate by the well-known gravimetric methods.[1]

Estimation of Chlorine (Bromine, Iodine)

Fats bleached by means of chlorine may retain small quantities of the bleaching agent.

Benedikt and *Zikes*[2] determine small quantities of chlorine by allowing 25 grms. of the sample under examination to drop slowly from a separating funnel into a combustion tube filled with lime.

The estimation is then carried out in the well-known manner of determining chlorine in organic substances.

In the same way bromine and iodine would be determined which occur legitimately in brominated and iodised fats (cp. chap. xv.; also Cod Liver Oil).

[1] Cp. Louise, *Compt. rend.* 129 (1899), 394; *Journ. Pharm. Chim.* 10, 241. Fränkel, *Pharm. Post*, 34 (1901), 117.

[2] *Journ. Soc. Chem. Ind.* 1894, 984.

CHAPTER V

PHYSICAL METHODS OF EXAMINING OILS, FATS, AND WAXES

THE examination of the physical properties of oils, fats, and waxes affords, in many cases, valuable information, and lends important aid in the identification of samples, and in the detection of adulteration.

The specific gravity of the oils, fats, and waxes, and the melting and solidifying points of their fatty acids furnish, as a rule, the most valuable and useful criteria.

The determination of the refractive index has become, following on the construction of handy apparatus, one of the readiest means of preliminary examination for purity of samples, and whenever the necessary apparatus is available it should be employed, as frequently this method combines rapidity of observation with certainty of result.

In some cases, especially in the examination of lubricating oils, the determination of the viscosity will prove of some assistance.

The behaviour of oils and fats with solvents will often serve as a valuable confirmation of indications furnished by other tests. Considering the great similarity in the chemical composition of the individual oils and fats, the systematic employment of a series of solvents, with a view to differentiation, offers little hope of success.

Microscopic examination has recently come more to the fore and promises to offer great assistance in the detection of mixed glycerides.

A number of other physical properties and their determination will be referred to for the sake of completeness, although these determinations can hardly be carried out in an analytical laboratory.

The physical properties, and the methods of determining them, will be described under the following heads in the order of their importance from an analytical point of view, *i.e.* in the order of their utility for the identification of individual oils, and recognition of their purity :—

1. Specific Gravity.
2. Melting and Solidifying Points.
3. Refractive Index.
4. Viscosity.

5. *Rotatory Power.*
6. Microscopic Appearance (Micrography).
7. Spectroscopical Examination.
8. Consistence.
9. Solubility.
10. Electrical Conductivity.
11. Calorimetric Examination.

Some further methods have been omitted as being entirely useless, such as the determination of cohesion figures, emulsifying power, etc. Others, such as the determination of specific heat,[1] or of diffusion coëfficients,[2] or of capillary analysis,[3] have not been admitted here, as they do not lead to any more useful results than can be arrived at by less complicated methods.

1. Specific Gravity

The specific gravity of the **liquid** fats and waxes may be ascertained at the ordinary temperature by the well-known methods adopted for any other liquid, viz. by means of a hydrometer, picnometer, or the hydrostatic balance.

It should hardly be necessary to emphasise here the importance of making sure of the accuracy and delicacy of the hydrometer to be used. The readiest indications will be obtained by means of hydrometers referring to the density of water, whilst the use of *Twaddell's* hydrometer involves a calculation, simple though it be.

On the Continent and in America various hydrometers, based on an arbitrary scale, are used in commerce and still employed by the custom-house officials. These hydrometers, gauged for a certain temperature, express the densities in "degrees"; the real specific gravities s can be calculated by means of the subjoined table, n denoting the number of "degrees."

[1] Vandevyer-Grau, *Ann. Chim. anal.* 5, 321.
[2] Zaloziecki, *Chem. Rev.* 1897, 220, 229.
[3] Goppelsroeder, *Capillaranalyse*, Bale, 1901.

Hydrometer.	Temperature.	For Liquids heavier than Water.	For Liquids lighter than Water.
Balling . .	17·5° C.	$s=\frac{200}{200-n}$	$s=\frac{200}{200+n}$
Baumé I . .	12·5° C.	$s=\frac{144}{144-n}$	$s=\frac{144}{134+n}$
Baumé II . .	15° C.	$s=\frac{144 \cdot 3}{144 \cdot 3-n}$	$s=\frac{144 \cdot 3}{134 \cdot 3+n}$
Baumé III . .	17·5° C.	$s=\frac{146 \cdot 78}{146 \cdot 78-n}$	$s=\frac{146 \cdot 78}{136 \cdot 78+n}$
Beck . . .	12·5° C.	$s=\frac{170}{170-n}$	$s=\frac{170}{170+n}$
Brix . . .	{12·5° R. 15·625° C.	$s=\frac{400}{400-n}$	$s=\frac{400}{400+n}$
Cartier . .	12·5° C.	$s=\frac{136 \cdot 8}{126 \cdot 1-n}$	$s=\frac{136 \cdot 8}{126 \cdot 1+n}$
Fischer . .	{12·5° R. 15·625° C.	$s=\frac{400}{400-n}$	$s=\frac{400}{400+n}$
Gay-Lussac . .	4° C.	$s=\frac{100}{n}$	$s=\frac{100}{n}$
E. G. Greiner .	{12·5° R. 15·625° C.	$s=\frac{400}{400-n}$	$s=\frac{400}{400+n}$
Stoppani . .	{12·5° R. 15·625° C.	$s=\frac{166}{166-n}$	$s=\frac{166}{166+n}$
Twaddell . .	...	$s=\frac{\frac{n}{2}+100}{100}$	

Hydrometers should only be employed where rapidity is of greater importance than accuracy. In these cases the following tables will be found useful :—

Comparison of the Hydrometer Degrees, according to Baumé and Twaddell, with the Specific Gravities

Baumé.	Twaddell.	Specific Gravity.	Baumé.	Twaddell.	Specific Gravity.	Baumé.	Twaddell.	Specific Gravity.
0	0	1·000	6·7	10	1·050	13·6	21	1·105
0·7	1	1·005	7·0	10·2	1·052	14·0	21·6	1·108
1·0	1·4	1·007	7·4	11	1·055	14·2	22	1·110
1·4	2	1·010	8·0	12	1·060	14·9	23	1·115
2·0	2·8	1·014	8·7	13	1·065	15·0	23·2	1·116
2·1	3	1·015	9·0	13·4	1·067	15·4	24	1·120
2·7	4	1·020	9·4	14	1·070	16·0	25	1·125
3·0	4·4	1·022	10·0	15	1·075	16·5	26	1·130
3·4	5	1·025	10·6	16	1·080	17·0	26·8	1·134
4·0	5·8	1·029	11·0	16·6	1·083	17·1	27	1·135
4·1	6	1·030	11·2	17	1·085	17·7	28	1·140
4·7	7	1·035	11·9	18	1·090	18·0	28·4	1·142
5·0	7·4	1·037	12·0	18·2	1·091	18·3	29	1·145
5·4	8	1·040	12·4	19	1·095	18·8	30	1·150
6·0	9	1·045	13·0	20	1·100	19·0	30·4	1·152

Comparison of the Hydrometer Degrees, according to Baumé and Twaddell, with the Specific Gravities—continued

Baumé.	Twaddell.	Specific Gravity.	Baumé.	Twaddell.	Specific Gravity.	Baumé.	Twaddell.	Specific Gravity.
19·3	31	1·155	37·8	71	1·355	51·5	111	1·555
19·8	32	1·160	38·0	71·4	1·357	51·8	112	1·560
20·0	32·4	1·162	38·2	72	1·360	52·0	112·6	1·563
20·3	33	1·165	38·6	73	1·365	52·1	113	1·565
20·9	34	1·170	39·0	74	1·370	52·4	114	1·570
21·0	34·2	1·171	39·4	75	1·375	52·7	115	1·575
21·4	35	1·175	39·8	76	1·380	53·0	116	1·580
22·0	36	1·180	40·0	76·6	1·383	53·3	117	1·585
22·5	37	1·185	40·1	77	1·385	53·6	118	1·590
23·0	38	1·190	40·5	78	1·390	53·9	119	1·595
23·5	39	1·195	40·8	79	1·395	54·0	119·4	1·597
24·0	40	1·200	41·0	79·4	1·397	54·1	120	1·600
24·5	41	1·205	41·2	80	1·400	54·4	121	1·605
25·0	42	1·210	41·6	81	1·405	54·7	122	1·610
25·5	43	1·215	42·0	82	1·410	55·0	123	1·615
26·0	44	1·220	42·3	83	1·415	55·2	124	1·620
26·4	45	1·225	42·7	84	1·420	55·5	125	1·625
26·9	46	1·230	43·0	84·8	1·424	55·8	126	1·630
27·0	46·2	1·231	43·1	85	1·425	56·0	127	1·635
27·4	47	1·235	43·4	86	1·430	56·3	128	1·640
27·9	48	1·240	43·8	87	1·435	56·6	129	1·645
28·0	48·2	1·241	44·0	87·6	1·438	56·9	130	1·650
28·4	49	1·245	44·1	88	1·440	57·0	130·4	1·652
28·8	50	1·250	44·4	89	1·445	57·1	131	1·655
29·0	50·4	1·252	44·8	90	1·450	57·4	132	1·660
29·3	51	1·255	45·0	90·6	1·453	57·7	133	1·665
29·7	52	1·260	45·1	91	1·455	57·9	134	1·670
30·0	52·6	1·263	45·4	92	1·460	58·0	134·2	1·671
30·2	53	1·265	45·8	93	1·465	58·2	135	1·675
30·6	54	1·270	46·0	93·6	1·468	58·4	136	1·680
31·0	54·8	1·274	46·1	94	1·470	58·7	137	1·685
31·1	55	1·275	46·4	95	1·475	58·9	138	1·690
31·5	56	1·280	46·8	96	1·480	59·0	138·2	1·691
32·0	57	1·285	47·0	96·6	1·483	59·2	139	1·695
32·4	58	1·290	47·1	97	1·485	59·5	140	1·700
32·8	59	1·295	47·4	98	1·490	59·7	141	1·705
33·0	59·4	1·297	47·8	99	1·495	60·0	142	1·710
33·3	60	1·300	48·0	99·6	1·498	60·2	143	1·715
33·7	61	1·305	48·1	100	1·500	60·4	144	1·720
34·0	61·6	1·308	48·4	101	1·505	60·6	145	1·725
34·2	62	1·310	48·7	102	1·510	60·9	146	1·730
34·6	63	1·315	49·0	103	1·515	61·0	146·4	1·732
35·0	64	1·320	49·4	104	1·520	61·1	147	1·735
35·4	65	1·325	49·7	105	1·525	61·4	148	1·740
35·8	66	1·330	50·0	106	1·530	61·6	149	1·745
36·0	66·4	1·332	50·3	107	1·535	61·8	150	1·750
36·2	67	1·335	50·6	108	1·540	62·0	150·6	1·753
36·6	68	1·340	50·9	109	1·545	62·1	151	1·755
37·0	69	1·345	51·0	109·2	1·546	62·3	152	1·760
37·4	70	1·350	51·2	110	1·550	62·5	153	1·765

Comparison of the Hydrometer Degrees, according to Baumé and Twaddell, with the Specific Gravities—continued

Baumé.	Twaddell.	Specific Gravity.	Baumé.	Twaddell.	Specific Gravity.	Baumé.	Twaddell.	Specific Gravity.
62·8	154	1·770	65·0	164	1·820	67·0	173	1·865
63·0	155	1·775	65·2	165	1·825			
63·2	156	1·780	65·5	166	1·830			
63·5	157	1·785	65·7	167	1·835			
63·7	158	1·790	65·9	168	1·840			
64·0	159	1·795	66·0	168·4	1·842			
64·2	160	1·800	66·1	169	1·845			
64·4	161	1·805	66·3	170	1·850			
64·6	162	1·810	66·5	171	1·855			
64·8	163	1·815	66·7	172	1·860			

Degrees Baumé, for Liquids lighter than Water at 15·5° C. = 60° F.

Degrees Baumé.	Specific Gravity.	Degrees Baumé.	Specific Gravity.	Degrees Baumé.	Specific Gravity.	Degrees Baumé.	Specific Gravity.	Degrees Baumé.	Specific Gravity.
10	1·0000	24	0·9090	38	0·8293	51	0·7734	64	0·7216
11	0·9929	25	0·9032	39	0·8284	52	0·7692	65	0·7179
12	0·9859	26	0·8974	40	0·8235	53	0·7650	66	0·7142
13	0·9790	27	0·8917	41	0·8187	54	0·7608	67	0·7106
14	0·9722	28	0·8860	42	0·8139	55	0·7567	68	0·7070
15	0·9655	29	0·8805	43	0·8092	56	0·7526	69	0·7035
16	0·9589	30	0·8750	44	0·8045	57	0·7486	70	0·7000
17	0·9523	31	0·8695	45	0·800Q	58	0·7446	75	0·6829
18	0·9459	32	0·8641	46	0·7954	59	0·7407	80	0·6666
19	0·9395	33	0·8588	47	0·7909	60	0·7368	85	0·6511
20	0·9333	34	0·8536	48	0·7865	61	0·7326	90	0·6363
21	0·9271	35	0·8484	49	0·7821	62	0·7290	95	0·6222
22	0·9210	36	0·8433	50	0·7777	63	0·7253	100	0·6087
23	0·9150	37	0·8383						

Specific gravity is usually determined by means of a picnometer of one kind or another. Of these the ordinary specific gravity bottle, consisting of a plain flask with a stopper having a capillary perforation, will be found useful for commercial work, and with care, even the fourth decimal may be determined accurately.

A very high degree of accuracy is obtained by means of *Sprengel's* picnometer (Fig. 8). This is a U-tube made of thin glass, ending in two capillary tubes *a* and *b* bent at right angles and ground at their ends, so as to fit into two glass caps (the latter are not shown in the figure). The inner diameter of tube *b*, bearing the mark *m*, is about 0·5 mm., whilst that of tube *a* is less, and should not exceed 0·25 mm. This point should be noted, as this essential feature of the Sprengel tube is lost sight of by some makers. The tube is filled by connecting *a* with a glass bulb, and sucking the air out of

it by means of india-rubber tubing, whilst *b* is immersed in the oil under examination. If the glass bulb be chosen sufficiently large, the Sprengel tube will be filled automatically on closing the india-rubber tubing with the fingers. As soon as the oil enters the bulb the Sprengel tube is detached from it, and the picnometer allowed to assume the desired temperature (see below). It will be found that the liquid expands or contracts *in the tube b only, i.e.* in the direction of the least resistance, whilst the capillary tube *a* will always remain full. If the meniscus of the liquid is found to be beyond the mark *m*, a little of the oil can be abstracted by means of a roll of filter-paper applied to the end of *a*; if, however, the tube contains too little, *a* may be touched with a glass rod which has been dipped into the oil, thus allowing some to be sucked in by the capillary tube, the liquid moving forward in the tube *b*. In this manner the volume can be adjusted easily. Finally, the two glass caps are put on the tubes *a* and *b*, and the picnometer is then ready for weighing.

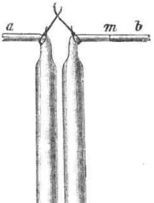


Fig. 8.

If the weights found be reduced to weights *in vacuo*, the fourth decimal in the specific gravity will be correct, the error only affect-

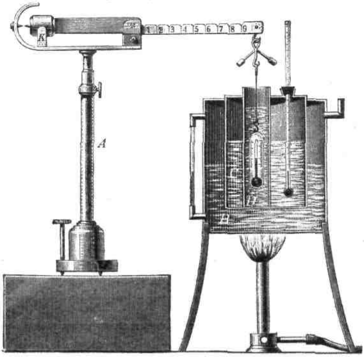


Fig. 9.

ing the fifth decimal. So high a degree of accuracy is but rarely required; in the technical analysis of glycerin (cp. chap. xv.), however, the Sprengel tube is frequently necessary.

Mohr's or the hydrostatic balance is not so accurate, but still quite satisfactory for ordinary purposes, and is largely used on account of the convenience and rapidity of the operation. One form of this instrument is shown in Fig. 9, and requires no further explanation.[1] The plummet, it may be added, displaces exactly 10 c.c., and therefore the weights put on the lever to restore equilibrium are exactly the weight of 10 c.c. of the substance. Thus all calculation is avoided, the specific gravity being read direct from the weights used.

For the determination of viscous oils (such as boiled oils) at the ordinary temperature, the picnometer described by *Brühl* (Fig. 10) is useful. A pipette containing the viscous substance is inserted air-tight in the flask by means of an india-rubber tube, and the air exhausted by connecting the side tube with a filter pump.

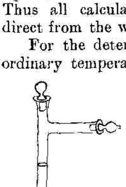


Fig. 10.

In specific gravity determinations, care must be taken to ensure the equal temperature of the oil throughout its entire mass. For this purpose it will be found best, after having brought the oil to the standard temperature, to keep it for some time—10 minutes at least—in a sufficiently large water-bath having the same temperature. The temperature should be observed by means of an accurate thermometer. The standard temperature in this country is 60° F. = 15·5° C.

The weight of the volume of oil should be compared with that of an equal volume of water taken at the same temperature. It is customary to consider the weight of that volume of water at 15·5° C. as unity. In exact work the weight should be reduced to that *in vacuo* and referred to water at 4° C. (cp. "Glycerin," chap. xv.).

If the quantity of oil under examination is too small to fill a picnometer, the specific gravity may be ascertained from that of a dilute alcohol, in which a drop of the oil will just float (cp. p. 166).

Obviously, the determination of the specific gravity of those fats and waxes that are semi-solid at the standard temperature, leads to complications and difficulties (see below). They are avoided by adopting as the standard a convenient temperature at which the substances are in a fluid state. *Bell* and *Muter* somewhat arbitrarily proposed the temperature of 100° F. = 37·75° C., whilst others prefer the temperature of boiling water.

For correct determinations it will be found best to use a Sprengel tube. The tube is immersed in boiling water in such a manner that only the ends of the capillary tubes protrude. After about twenty minutes' boiling the glass caps are placed on the tubes, the Sprengel tube is removed from the water-bath, wiped dry, and weighed after cooling. The weight of the fat may be referred to the weight of water at the boiling point, or, as has been done by most observers,

[1] Cp. Thörner, *Journ. Soc. Chem. Ind.* 1895, 44 (Illustration).

to the weight of water at 15·5° C. The unity chosen must, of course, be distinctly stated. The scientific method would be to take water at 4° C. as unity.

Whilst the hydrostatic balance will be found very convenient at the ordinary temperature, its employment at higher temperatures necessitates the use of a somewhat complicated arrangement. The one recommended by *Bell* is shown (partly in section) in Fig. 9. *It is designed for the temperature of 100° C.* *D* is a glass tube containing the sample of fat; C is filled with paraffin wax, and is surrounded by the water-jacket B.

In cases where, for some special reason, neither the temperature of 15·5° C. nor 100° C. can be employed, a correction must be made, depending on the coëfficient of expansion of the particular oil under examination. *Allen*[1] has determined the rate of expansion of a number of fats, by taking their densities at 98° C. and 15·5° C., and dividing the difference of the densities by the difference of the temperatures. Thus he obtains the correction to be made for a variation of 1° C. Although this method is not scientifically correct, inasmuch as it rests on the assumption that the rate of expansion does not vary between 15·5° C. and 98° C. [the mean coëfficient of expansion differs from the true one as the quotient of differences from the differential quotient], the values obtained by *Allen* will satisfy practical requirements. Excepting whale oil, which exhibits an *abnormal rate of expansion, the correction for 1° C. has been found* to vary for seventeen kinds of fats between the limits 0·000615 and 0·000665. Therefore *Allen* proposes to take as the mean correction for one degree Celsius 0·00064 (or for one degree Fahrenheit 0·00035). Thus, if the density of an oil is 0·9207 at 22° C., its density at 15·5° C. will be found by the following calculation. The difference of the temperatures is $22 - 15·5 = 6·5$; the correction is therefore $6·5 \times 0·00064 = 0·00416$. This figure added to 0·9207 gives 0·92486 as the specific gravity at 15·5° C.

The coëfficient of expansion of an oil may also be found by this "picnometric method" by dividing the correction for one degree of temperature by the specific gravity of the oil at the lower temperature. But it should be borne in mind that the volume of the picnometer varies with the temperature, and that it is therefore necessary to make a correction for the expansion of the glass.

In the determination of the specific gravity of **solid** *fats and* waxes, it is convenient to use a temperature at which they are liquid, say 100° C. At the ordinary temperature *Gintl's*[2] picnometer, shown in Fig. 11, may be found useful. It consists of a small cylindrical, flat-bottomed vessel, *I*, made of very thin glass and provided with a ground-glass cover. The vessel fits into the frame *a* (Fig. 12), the screw *b* serving to press the glass cover tightly on the cylinder. The vessel is weighed first empty and then filled with water at the

[1] *Commercial Organic Analysis*, ii. 19.
[2] *Dingl. Polyt. Journ.* 194. 42.

standard temperature. After emptying the water and drying carefully, *I* is filled with the melted fat completely, and allowed to cool to the standard temperature. The glass cover is then carefully placed on *I*, so that the surplus fat is squeezed out, and secured in its position by means of the screw. The fat on the outside is washed off with ether and the vessel is then weighed again.

Another method proposed originally by *Fresenius* and *Schulze* will be found useful in the case of waxes. This method is best employed in the form given it by *Chattaway* and *Allen*.[1] The wax is melted on a watch-glass placed on boiling water, and small pieces are cut from the *spontaneously* cooled mass. They are next brushed over with a wet brush in order to remove adherent air-bubbles, and carefully

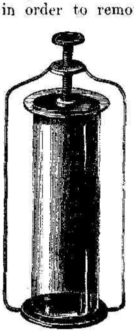


Fig. 11.

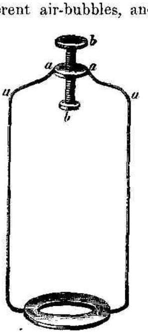


Fig. 12.

placed in dilute alcohol by means of a pair of forceps. It is convenient to keep a set of standard mixtures of alcohol and water, having the specific gravities at 15·5° C., say of 0·960, 0·961, 0·962, and so on up to 0·970. That liquid in which the wax globules will just float furnishes the specific gravity of the sample.

A somewhat complicated apparatus for the determination of the densities of soft fats has been proposed by *Zawalkiewicz*.[2]

Instead of determining the specific gravity by weighing a definite volume according to the formula $d = \frac{m}{v}$ (where *d* denotes the density, *v* the volume, and *m* the weight), *Zaloziecki*[3] proposes to measure the volume of the fatty acids derived from a known weight of fat. Evidently this is no new constant, as from the formula just given it follows that $v = \frac{m}{d}$, and no further information is gained than that afforded by the determination of the specific gravity number of the fat. The volume of the fatty acids is referred to the weight of fat, and

[1] *Commercial Organic Analysis*, ii. 184. [2] *Journ. Soc. Chem. Ind.* 1894, 839.
[3] *Chem. Revue*, 1897, 119.

it becomes therefore simply a question whether the method proposed by *Zaloziecki* is more expeditious than the weighing of the original fat in a picnometer. There can be no doubt that *Zalozieckl's* method is more cumbersome. For this reason, and for the more cogent one that a serious error is introduced by the solubility of the volatile fatty acids, this method cannot be recommended.

Although the specific gravity of the individual oils, fats, and waxes furnishes an important and characteristic number, serving frequently as an additional means of identification, or as a verification of results arrived at by other methods, the specific gravity numbers in themselves are of very little discriminating value for purposes of classification. Hence, the importance that has been ascribed to the specific gravity numbers in earlier works on our subject (at a time when the chemical examination of fats had not been worked out so fully as at present) was much overrated. This may be exemplified by the extensive use of "oleometers" purporting to discriminate not only between different oils, but even to detect adulteration. To indicate that the specific gravity alone is of limited value as a sorting test, I append the following table, in which I have placed the specific gravities of some oils and fats against the classes adopted in this treatise :—

Specific Gravities of Oils,

	0·876-0·883	0·900-0·910	0·913-0·916	0·916-0·920
FATTY OILS :—				
Vegetable oils—				
Drying oils	...	...	...	...
Semi-drying oils	...	...	Rape oil group	...
Non-drying oils	...	...	...	Almond oil, arachis oil, *olive* oil, etc.
Animal Oils :—				
Marine animal oils—				
Fish oils	...	Sun fish oil, cramp-fish oil (?)	...	Japan fish oil
Liver oils	...	...	...	...
Blubber oils	...	...	...	...
Terrestrial animal oils	...	...	Egg oil, neat's *foot oil*, sheep's horse's	foot oil foot oil
SOLID FATS :—				
Vegetable fats	...	...	...	...
Animal fats—				
Drying fats	...	...	...	...
Non-drying fats	...	...	Bone fat	Wild goose fat, horse fat
LIQUID WAXES	*Sperm oil*, arctic sperm oil			
SOLID WAXES :—				
Vegetable waxes	...	...	...	...
Animal waxes	...	...	...	...

Fats, and Waxes, at 15° C.

0·920-0·925	0·925-0·935	0·935-0·940	0·940-0·950	0·950-0·960	0·960-0·970	0·970-0·999
...	Linseed oil, hemp seed oil, etc.	... Tung	oil			
Maize oil, cotton seed oil, sesamé oil, etc.						
...	...	...	...	Castor oil, croton oil		
Herring oil, menhaden oil, etc.						
Cod liv skate li e	er oil, ver oil, tc.					
...	Whale oil, porpoise oil					
Palm oil, macassar oil	Laurel oil	...	Nutmeg	butter	...	Japan wax, myrtle wax
				Cacao	butter	
...	Hare fat, wild rabbit fat, etc.					
...	...	Lard	...	...	Stag fat, chamois fat, etc.	
		Tal	low			
...	...	...	...	...	...	Carnaüba wax
...	...	...	...	...	Beeswax, insect wax	

Although the liquid waxes on the one hand, and the solid waxes (including the wax-like fats) on the other hand, may readily be recognised by their specific gravities, still much overlapping will be noticed. Some oils and fats fall within more than one subdivision, and the most heterogeneous fats, as regards chemical composition and other properties, arrange themselves in one and the same vertical column. It is therefore unnecessary to give here a complete list of the specific gravities. These will be found in Chapter XIV., under the heading of each individual oil, fat, or wax. A complete enumeration of the specific gravities, furnishing a rapid survey of individual oils, fats, and waxes, is contained in Tables 24 of my "*Laboratory Companion.*"

The basis of the classification adopted throughout this treatise being the iodine value, it may be interesting to inquire whether any definite connection can be traced between the iodine value and the specific gravity. Since a higher iodine value indicates a higher amount of unsaturated glycerides, and since the greater the unsaturation of the fatty acids, the higher is their specific gravity, some parallelism may be expected. Speaking broadly, such an one may indeed be traced through the three classes of oils, the drying, semi-drying, and non-drying oils. But due regard must also be paid to the chemical constitution of the fatty acids, since castor oil entirely deviates from the rough approximation to the general rule which the several classes just mentioned seem to follow. Still less regularity can be expected, as even differences of climatic conditions, of race, etc., produce a difference in the specific gravity, as well as in the iodine value. *Wijs* has endeavoured to trace a correspondence between the specific gravity and the iodine value in the case of linseed oil, sesamé oil, and arachis oil. Whereas in these cases high specific gravities seem to correspond to high iodine values, the rule seems to break down in the case of cotton seed oil. More information on this subject will be found under each individual oil in Chapter XIV.

The influence of glycerides of soluble fatty acids on the specific gravities of some solid fats is shown by the following two tables. It will be seen that the presence of glycerides of soluble acids increases the specific gravity number.

A. *Fats, Free from Glycerides of Soluble Fatty Acids*

Class of Fat.	Kind of Fat.	Specific Gravities at 100° C. (Water at 15° C. = 1.)
Vegetable Fats . . .	Cacao butter	0·857
	Palm oil	0·857
	Japan wax	0·8755
Animal Fats . . .	Lard	0·861
	Tallow (beef and mutton)	0·860
	Horse fat	0·861
	Oleomargarine	0·859

B. *Fats, containing Glycerides of Soluble Fatty Acids*

Class of Fat.	Kind of Fat.	Specific Gravities at 100° C (Water at 15° C. = 1.)
Vegetable fats . . .	Cocoa nut oil Palm nut oil	0·8736 0·8731
Animal fats	Butter fat	0·865-0·868

The presence of free fatty acids in oils and fats naturally influences the specific gravity number to some extent, so that the specific gravity rises with the increase of free fatty acids. A definite relation, however, does not exist between the amount of free fatty acids and the specific gravity. This is shown by the numbers contained in the following table:—

No.	Kind of Oil.	Free Fatty Acids. Per cent.	Specific Gravity at 15·5° C. (Water at 15·5° C. = 1.)	Observer.
1	Olive oil, No. 2, freed from fatty acids	0·0	0·9152	Thomson and Ballantyne[1]
2	Olive oil	3·86	0·9148	,, ,,
3	Olive oil (edible)	4·15	0·9151	,, ,,
4	Olive oil	5·19	0·9168	,, ,,
5	Olive oil (Gioja)	9·42	0·9156	,, ,,
6	Olive oil (for dyeing)	9·67	0·9154	,, ,,
7	Olive oil	11·28	0·9145	,, ,,
8	Olive oil	19·83	0·9160	,, ,,
9	Olive oil	23·78	0·9147	,, ,,
10	Olive oil, from bagasse	71·12	0·9277	Klein[2]
11	Sulphur olive oil, Italian	48·2	0·9197	Lewkowitsch[3]
12	Sulphur olive oil, Italian	49·4	0·9204	,,
13	Sulphur olive oil, Syrian	64·2	0·9193	,,
14	Olive oil, Californian	12·11	0·9149	Tolman and Munson[4]

In order to obviate the uncertainty attaching to the determination of the specific gravity of oils containing free fatty acids, *Archbutt* proposed to take the specific gravities of the liberated fatty acids. Most fatty acids being solid at the standard temperature, the determinations must be made at the boiling point of water, but the meagre information so obtained will hardly repay the trouble entailed.

The changes in specific gravity which are brought about by rancidity are shown in the following table due to *Thomson* and *Ballantyne*,[5] which embodies the results obtained on exposing some oils to the action of direct sunlight in uncorked bottles, the contents of which were agitated every morning for six months:—

[1] *Journ. Soc. Chem. Ind.* 1890, 589. [2] *Ibid.* 1898, 1055. [3] Unpublished notes.
[4] *Journ. Amer. Chem. Soc.* 1903, 957. The average specific gravity of Californian oils was found 0·9168.
[5] *Journ. Soc. Chem. Ind.* 1891, 30. Cp. also Sherman and Falk, *Journ. Amer. Chem. Soc.* 1903, 711.

Kind of Oil.	Specific Gravity at 15·5° C. (Water at 15·5° C.=1.)						
	Original.	After 1 Month.	After 2 Months.	After 3 Months.	After 4 Months.	After 5 Months.	After 6 Months.
Olive . . .	0·9168	0·9187	0·9193	0·9208	0·9215	0·9227	0·9246
Castor . .	0·9679	0·9681	0·9691	0·9700	0·9700	0·9685	0·9683
Colza . . .	0·9168	0·9183	0·9172	0·9185	0·9184	0·9200	0·9207
Cotton seed .	0·9225	0·9237	0·9241	0·9261	0·9278	0·9304	0·9320
Arachis . .	0·9209	0·9213	0·9221	0·9233	0·9239	0·9256	0·9267
Linseed . .	0·9325	0·9331	0·9336	0·9353	0·9359	0·9372	0·9385

2. Melting and Solidifying Points

Various methods have been proposed for the determination of the **melting points** of fats, but unfortunately they lead to discordant results. Nor is this to be wondered at if we remember that natural oils and fats are not definite chemical substances, characterised by a definite melting point, but are mixtures of a number of glycerides. A further complication arises from the fact that even pure glycerides, such as trimyristin, tripalmitin, and tristearin, present in their melting points irregularities such as are not shown, as a rule, by definite chemical substances. It has been shown above that even the pure triglycerides have apparently two melting points, a fact which up till recently was looked upon as proving that the triglycerides occur in two physical modifications; as shown above, a satisfactory explanation has been given by *Guth* (see p. 9). Hence, in determining the melting point of a pure glyceride, one should endeavour to examine it in the *crystalline state only*.

In the case of commercial oils and fats, the crystalline form cannot be obtained, so that they do not melt sharply at a definite degree of temperature, but soften first, and only melt to a clear liquid after further heating.

There is also a good deal of uncertainty as to which of the two temperatures should be taken as the melting point, whether that at which a fat commences to liquefy, or that at which it has become perfectly transparent. Some experimenters identify the melting point with the temperature at which the fat undergoes a certain degree of softening, either sufficient to permit a plug of fat, contained in a glass tube open at either end, to be forced up by the hydrostatic pressure of water, or to allow the fat to form a globule.

The want of a uniform method for the determination of the melting point is therefore much felt, and one that would command general acceptance is still a desideratum, for in the valuation of some commercial fats (such as chocolate fats) considerable importance attaches to the melting point.

It should be borne in mind that fats do not exhibit their normal melting point shortly after being melted. It is only recovered after the lapse of a day or two; therefore if a sample has been melted it should be allowed to stand some time before the melting point is determined.[1]

On the Continent *Pohl's* method is largely employed. It consists in ascertaining the temperature at which a fat is just becoming liquid, although it may still retain solid particles. The bulb of a mercury thermometer is immersed in the melted fat and quickly removed, so that only a thin coating of fat adheres to it. After a day or two the thermometer is fixed in a long and wide test-tube by means of a cork, so that the bulb is still at a distance of about half an inch from the

[1] Cp. Cacao butter.

bottom. The test-tube is then fastened in a clamp and gently warmed by the heat radiating from a heated sheet of iron or asbestos placed below it at a distance of about one inch. The temperature is allowed to rise only very gradually. The moment a drop of liquid fat is observed to form at the bottom of the bulb, the temperature is read off and recorded as the melting point.

A somewhat modified form of the same method has been introduced by *Redwood.* A minute quantity of the melted fat, nearly cooled to its solidifying point, is placed by means of a thin glass rod on clean mercury contained in a small dish, and allowed to solidify. The dish may be placed in a beaker containing water, which is heated very gradually. A thermometer is dipped in the mercury, and that temperature at which the fat spreads over the mercury is recorded as the melting point. This method can be recommended; it is, however, preferable to place a somewhat large quantity of the not previously melted fat on the surface of the mercury.

Frequently the melting point is ascertained in capillary tubes, such as are usually employed for organic substances.[1] The "Society of Bavarian Analytical Chemists" have agreed upon the following *modus operandi*:—Draw up the melted fat into a thin-walled capillary tube 1 or 2 cm. high, corresponding to the length of the bulb of the thermometer to be used; seal one end of the tube, and attach the latter to the stem of the thermometer in such a way that the substance and the mercury bulb are at the same level. After an interval of about twenty-four hours immerse the thermometer in glycerin contained in a test-tube about an inch and a half wide, and heat the liquid very gently. The temperature at which the thin cylinder of fat has become perfectly clear and transparent should be considered as the melting point.

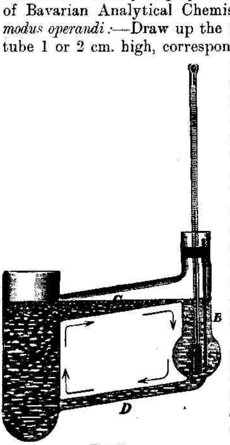


Fig. 13.

An apparatus adapted for this method, designed by *Olberg*, is shown in Fig. 13. The vessel is filled with oil, and on this being heated at A a natural circulation takes place without requiring any stirring.

From the explanation given above (chap. i.) for the occurrence of two melting points of the pure glycerides, it will be seen that the capillary tubes must not be chosen too narrow. Unless attention be paid to this point, differences amounting to several degrees may be found between the methods of determining the melting point on

[1] Cp. T. Tyrer and A. Levy, *Pharm. Journ.* 1899, July 29.

mercury and in capillary tubes, the differences increasing as the diameter of the capillary decreases. The determination of the melting point of fats in capillary tubes is therefore to be used with caution only. The uncertainty attaching to the determination of the melting point in capillary tubes has led *Bensemann*[1] to determine two points, viz. the point of *incipient fusion* and the point of *complete fusion*.

Since this method is still largely used on the Continent, it may be described here in full. A drop of the melted fat is placed in a tube as shown in Fig. 14, *a*, and allowed to solidify in such a position that it forms a globule at A. The tube is then attached to a thermometer and immersed in water contained in a beaker. By gently warming the water over a very small flame a point is reached when the fat just begins to flow down the side of the tube. The temperature at which this takes place is recorded as the "point of incipient fusion." The drop of fat will then have taken the position shown in *b*. By further application of heat the drop becomes at last completely transparent; the corresponding temperature is the "point of complete fusion." The difference between these two points is about 3° to 4° C.

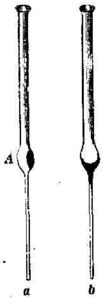


Fig. 14.

Several chemists have proposed an acoustical method for ascertaining the melting point of fats. The principle on which an apparatus of this kind is based is the following:—Two platinum wires connected to a battery and an electrical bell are immersed in the solid fat. On the latter becoming melted the circuit is closed, and this moment is indicated by the ringing of the bell. The first apparatus of this kind was designed by *Loewe*, and has been modified in some minor points by *Jean*. The essential part of *Jean's* apparatus consists in a U-tube, into which a quantity of the melted fat, sufficient to fill the bend of the tube, is poured. Two platinum wires are then introduced into the solidified fat down each limb of the tube, and connected with a battery and an electric bell. Next a little mercury is poured into one of the limbs of the tube, and the latter placed in a water-bath. On the fat becoming melted the mercury will fall through it, thus closing the circuit.

Another apparatus of the same type has been designed by *Christomanos*.[2] It is shown in Fig. 15.

The acoustical methods would appear, from a practical point of view, to entail too much trouble in commercial work, and considering the small amount of information that is gained, even from the correct determination of a melting point, it must be considered an over-elaboration of a method, to which recourse can be had only in exceptional cases.

[1] *Journ. Soc. Chem. Ind.* 1885, 535. [2] *Ibid.* 1890, 894.

Recently *Le Sueur* and *Crossley*[1] proposed to determine the melting point in the following manner:—Place in a thin-walled tube, about 75 mm. long and 7 mm. wide, a fine capillary tube, open at both ends, and protruding over the thin-walled tube. The diameter of the capillary should not exceed $\frac{3}{4}$ mm. A small portion of the fat under examination is then introduced into the thin-walled tube, so as to well cover the lower part of the capillary. The whole is then attached to the stem of the thermometer by means of two india-rubber bands placed in a beaker containing the heating fluid. That temperature at which the liquid is seen to rise in the capillary tube is noted as being the melting point of the fat. Whereas this method gives accurate results in the case of pure chemical substances, it did not give reliable results in my laboratory in the case of fats. Two defects are inherent to this method. The one is the tendency to give too low a melting point, in the case of fats containing glycerides of lower fatty acids, such as a butter fat and cocoa nut oil, owing to a portion of the fat having liquefied and rising in the capillary tube, whilst the remainder has not yet been melted. The second error is due to the viscosity of fats and plays an important part, in such cases as tallow, wool fat, and chocolate fats, when the melting points are found too high. The following table reproduces some of the results obtained in my laboratory:—

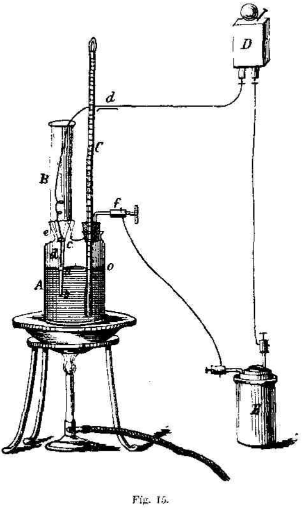


Fig. 15.

[1] *Journ. Soc. Chem. Ind.* 1898, 988.

[TABLE

Comparative Determinations of Melting Points of some Fatty Substances

Fat.	Le Sueur and Crossley's Method.			Ordinary Capillary-tube Method.	Hydrostatic Pressure Method.
	Softens in Outer Tube at	Clear in Outer Tube at	Rises in Capillary Tube at		
	°C.	°C.	°C.	°C.	°C.
Wool fat	...	...	45·6	36·7–39·2	32·4
			45·6	36·5–39·2	
			45·6		
	32	40	45·7	37·1–39·8	30·2–31·8
			45·4	37·4–39·8	
			45·7		
Butter	...	36	25·7–25·8	32·0–33·4	
			25·7–25·8	32·0–33·45	
Cocoa nut oil	...	26	22·8	24·8–25·2	
			23·2	24·8–25·2	
Stearolactone	...	39·1	34·8	37·0–37·7	
Tallow	...	...	45·4	41·1–45·0	
"*Chocolate fat*"—I.	...	...	34·4	28·3–28·5	
"Chocolate fat"—II.	...	...	35·5	28·3–28·5	

As will be seen from the preceding remarks, the exact determination of the melting point of a fat is attended with difficulties; moreover, some time must elapse before a sample can be tested.

For purposes of discriminating between various oils, the melting point has, as a rule, little analytical value. It is therefore unnecessary to add here tables enumerating the melting points of oils. In special instances, however, such as in the valuation of "winter oils," the melting point may acquire considerable importance.

Of somewhat greater importance is the determination of the melting points of solid fats, as it is frequently required to value various specimens of one and the same fat, according to their melting points. As has been explained above, the various methods in vogue yield different results. *An agreement between analytical chemists as to* an exact method is desirable. A table in which the various melting *points were set out would show so glaring a disagreement between* various observers, that for practical purposes I consider it useless to collate the numbers here. The melting points will be detailed fully under the heading of the various fats.

It should be noted that small amounts of free fatty acids influence the melting point to a considerable extent.

Less uncertainty attaches to the melting point of the mixed fatty acids derived from an oil or fat; therefore, in examining a sample of fat for commercial purposes, the **melting point of the liberated fatty acids** is usually taken. The melting points of the mixed fatty acids of the individual oils and fats will be found in Chapter XIV.

When melted substances **solidify**, the "latent heat of fusion" is liberated and a rise of temperature takes place. Whereas fatty acids

show this rise most distinctly, it is not so well marked in the case of fats. They are rather characterised by the temperature remaining constant for some time before further falling.

Rüdorff has studied the **solidifying points** of fats with a view to employing them as characteristics in the examination of fats. His method was to melt a fat and to agitate it continually with a thermometer, noting the temperature from time to time. He found that in the case of some fats the temperature fell to a certain point, remained constant thereat for a time, and then fell again. During the period the temperature remained constant the fat solidified; this temperature he considered to be the solidifying point.

In the case of other fats again, on solidification setting in, a fall of temperature takes place with a subsequent rise until a maximum is reached, and then the temperature remains constant until the mass has become solid throughout.

A number of other fats, finally, such as beef and mutton tallow, have no solidifying point proper, the temperature rising a few degrees, but not remaining constant. These fats behave like mixtures, part of which has become solid whilst the remainder is still liquid.

It is therefore not recommended to determine the solidifying point of fats; it is far preferable to examine the **fatty acids** instead of the fats themselves.

Dalican has proposed a method for the determination of the solidifying point of fatty acids, which has been adopted in this country, in the United States, and in France for the commercial examination and valuation of fats. It is known under the name of "Titer Test," and gives, as I can testify from my own experience, reliable and, in repeated observations, constant results, provided the test is made under exactly the same conditions. 100 grms. of the fat under examination are saponified (cp. p. 62), the separated fatty acids freed from water and finally filtered through a dry plaited filter into a porcelain dish. They are allowed to solidify and to stand over night under a desiccator. The fatty substance is then carefully melted in an air-bath or over a free flame, and as much of it poured into a test-tube, 16 cm. long and 3·5 cm. wide, as will fill the tube more than half full. The tube is then fastened by means of a cork into a wide-mouthed bottle, 10 cm. wide and 13 cm. high, and a delicate thermometer, indicating one-tenth of a degree, inserted in the fatty acids, so that the bulb reaches the centre of the mass. When a few crystals appear at the bottom of the tube, the mass is stirred by giving the thermometer a rotary movement, first three times from right to left, and then three times from left to right. Next stir continually, by giving to the thermometer a quick circular movement, without allowing it to touch the sides of the vessel, but taking care that all solidified portions, as they form, are well stirred into the mass. The mass will gradually become cloudy throughout. The thermometer must now be observed carefully. A good plan is

to write down the temperature at short intervals. At first the temperature will continue to fall, but then it will rise suddenly some tenths of a degree and reach a maximum, remaining thereat stationary for some little time before it falls again. This point is called the "**titer**" **or solidifying point.**

Finkener[1] does not consider this a satisfactory method, whereas in the opinion of the writer, it forms a reliable basis for the commercial valuation of solid fats, provided the fatty acids have been dried in the manner described. *Finkener* uses larger quantities in small globular flasks of about 50 mm. diameter, and in order to prevent rapid cooling he places the vessels filled with the melted acids in a wooden box[2] (Fig. 16). (The same apparatus is also recommended by him for the determination of the solidifying points of different kinds of tallow.) The solidifying points found by *Finkener* are higher than those obtained by *Dalican*, who did not lay sufficient stress on having the fatty acids dry. *Finkener's* apparatus has been adopted by the German Custom House officials.

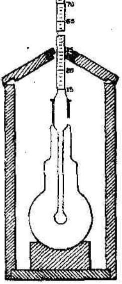


Fig. 16.

Higher solidifying points—by 0·2° to 0·3° C.—are obtained when the fatty acids are previously heated for two hours at 100° C. as proposed by *Wolfbauer*.[3] His method has been adopted in Austria for the determination of the titer test of tallow and palm oil, and I therefore describe it in full, although it suffers somewhat from over-elaboration.

120 grms. of the fat are melted in a beaker at a temperature but slightly above its melting point, mixed with 45 c.c. of caustic potash solution (1250 grms. of caustic potash in one litre of water), and stirred until the fat is completely emulsified. It is then covered and kept at 100° C. for two hours, being occasionally stirred. A small portion is then tested by warming with 50 per cent alcohol to ascertain whether saponification is complete; this is the case when a clear solution results. The soap is now decomposed by boiling with 165 c.c. of dilute sulphuric acid, sp. gr. 1·142, preferably in a silver dish, until the free fatty acids rise to the top as a clear oily layer. The silver dish is covered with an evaporating dish filled with cold water, to check the evaporation. The aqueous solution is then completely drawn off, and the fatty acids are washed by boiling one-quarter of an hour with dilute sulphuric acid (5 c.c. of concentrated sulphuric acid and 100 c.c. of water). After settling and removing the dilute acid, they are boiled with 100 c.c. of pure water; this last operation is repeated until the washings are no longer acid. The fatty acids are then dried in an open dish at 100° C. for two hours.

In the determination proper the following apparatus is

[1] *Journ. Soc. Chem. Ind.* 1889, 424. [2] *Ibid.* 1890, 1071.
[3] *Ibid.* 1894, 181. 908.

employed: a thin-walled test-tube, 3·5[1] cm. by 15 cm. is fixed by means of a cork in a suitable bottle. A centigrade thermometer, extending from 1° to 60° C., and graduated in fifths of a degree, is fixed in the test-tube by means of a cork, which must be sufficiently loose to permit of easy stirring of the contents of the tube with the thermometer. As the thermometer should be as short as possible, its scale is shortened by an enlargement blown in the bore in the interval between 2° and 28° C. The amount of mercury *above* the surface of the fatty acid is thus diminished, and an appreciable error thereby avoided. The test-tube is then filled to within 1 cm., or 1½ cm., of the top with the melted fatty acid, the thermometer immersed in the liquid to about the 35° mark (when the instrument should clear the bottom of the tube by about 4 cm. or 5 cm.), and the liquid stirred until it becomes quite opaque, and partial solidification sets in. Care should be taken at this point that the thermometer be not more deeply immersed, and after stirring rapidly in a circle ten more times, the temperature is observed. The mercury now begins to rise; the highest temperature noted may be taken as the solidifying point.

The reading of the thermometer should be corrected for its inherent errors, which should have been previously determined. Its zero point should also be redetermined from time to time. Each determination should be repeated, and the difference between the two should not exceed 0·1° C.; as a rule, it will not exceed 0·05° C.[2]

For reasons explained above it might appear doubtful whether *Wolfbauer's* higher values are due to removal of the last traces of adhering moisture, or to such slight changes of the fatty acids as are unavoidable whilst drying. But this doubt has been removed by the fact that *Shukoff* has obtained practically the same numbers by a method in which heating of the fatty acids is avoided.

Shukoff proposed at first to determine the "titer test" in a tube 3 cm. in diameter, surrounded by a Dewar vacuum mantle; the outer diameter of which is 5 cm. and the height 10 cm. The fatty acids are poured into the inner tube, which is then closed by a cork fitted with a delicate thermometer. About 5° above the expected "titer," the vessel is agitated in an up-and-downward direction somewhat energetically, until the contents have become distinctly turbid. The observation is then made in the manner described above. Later on *Shukoff*[3] showed that the vacuum mantle can be dispensed with, and that equally good results are obtained, if a tube of 2½ to 3 cm. diameter is fitted with a thermometer, and the whole is then fixed by means of a cork in a wide-mouthed bottle. The results so obtained are stated to be in close agreement with the numbers obtained by *Wolfbauer's* procedure.

[1] In a narrower tube, say 2·5 cm. diameter, the solidifying point was found to be lower by 0·20° C.

[2] For *Garrigues'* "method" cp. *Journ. Soc. Chem. Ind.* 1895, 280.

[3] *Chem. Ztg.* 1901, 99.

It goes without saying that by varying the conditions under which the "titer test" is taken, different results will be obtained. Therefore it is not so necessary to work out a new method as to agree on a certain *modus operandi*, and to strictly adhere to it. In my own experience, extending over a long number of years, *Dalican's* method, with the modifications described above, has proved itself reliable, and even different observers in my laboratory did not obtain greater variations than about 0·1 degree. This is quite satisfactory in consideration of the fact that in contracts an allowance is stipulated only for a divergence of over 0·2° C. from the guaranteed figure. Since *Dalican's* method has been made the basis of commercial transactions in this country, the United States, and France, new proposals for determining the titer, however acceptable otherwise, have little chance of superseding the established method.

The following table gives a list of "titer tests" collated from a very large number of observations made by the writer :—

Titer Tests of Mixed Fatty Acids (Lewkowitsch)

Class of Oil.	Kind of Oil.	Titer Test.	Remarks.
Drying oils	Linseed oil	20·6	
	Tung oil	37·2	
	Hemp seed oil	16·6	
	Poppy seed oil	16·2	
Semi-drying oils	Cotton seed oil	32·0	Lowest
	,, ,,	35·2	Highest
	Maize oil	19·0	
	Sesamé oil	23·8	
	Curcas	28·0	
	Rape oil	13·6	
	Croton	19·0	
Non-drying oils	Peach kernel oil	13·5	
	Almond oil	11·8	
	Arachis oil	29·2	
	Olive oil	17·2	Lowest
	,, ,,	26·4	Highest
Marine animal oils	Japanese sardine oil	28·2	
	Cod liver oil	18·4	Lowest
	,, ,,	24·3	Highest
	Seal oil	15·9	
	Whale oil	23·9	
Terrestrial animal oils	Sheep's foot oil	21·1	
	Horse's foot oil	28·6	
	Neat's foot oil	26·5	

Titer Tests of Mixed Fatty Acids (Lewkowitsch)—continued

Class of Fat or Wax.	Kind of Fat or Wax.	Titer Test.	Remarks.
Vegetable fats	Chaulmoogra oil	39·6	
	Laurel oil	15·1	
	Margosa oil	42·0	
	Mowrah seed oil	40·3	
	Shea butter	53·8	
	Vegetable tallow[1]	45·2	Lowest
	,, ,,	53·4	Highest
	Palm oil, Bonny	35·9	
	,, Bassam	38·47	
	,, Lagos	43·925	
	,, Old Calabar	44·6	
	,, Salt Pond	44·475	
	,, New Calabar	45·55	
	,, Congo	45·05	
	Macassar oil	51·6	Lowest
	,, ,,	53·2	Highest
	Sawarri fat	47·0	
	Nutmeg butter	35·95	
	Cacao butter	48·27	
	Palm nut oil	20·5	Lowest
	,, ,,	25·5	Highest
	Cocoa nut oil, commercial	22·55	Lowest
	,, ,,	25·2	Highest
	,, Cochin	25·2	
	Japan wax	59·4	
Animal fats	Horse fat	33·7	
	Horse marrow	38·55	
	Lard	42·0	
	Beef tallow, English	38·7	Lowest
	,, ,, ,,	45·1	Highest
	,, ,, North American	41·1	Lowest
	,, ,, ,, ,,	44·15	Highest
	,, ,, South American	42·95	Lowest
	,, ,, ,, ,,	46·25	Highest
	,, ,, Australian	38·3	Lowest
	,, ,, ,,	43·3	Highest
	Mutton tallow, English	41·5	Lowest
	,, ,, ,,	48·3	Highest
	,, ,, Australian	42·35	Lowest
	,, ,, ,,	48·05	Highest
	,, ,, New Zealand	45·9	Lowest
	,, ,, ,, ,,	48·0	Highest
	Beef marrow	38·0	
Liquid waxes	Sperm oil	11·9	
	Arctic sperm oil	8·6	

The **solidifying or freezing (congealing) point of oils** is determined by means of freezing mixtures with which the tube containing the oil is surrounded. The thermometer is inserted in the tube by means of a cork; for convenience a thermometer is used the scale of

[1] Commercial.

which commences above the cork. The following table [1] gives the proportions of water and certain salts required for the preparation of some freezing mixtures :—

Substances used.	Parts per 100 of Water.	Freezing Point. °C.
Distilled water		0
Potassium nitrate	13	−2·85
Potassium nitrate Sodium chloride	13 3·3	−5·0
Barium chloride	35·8	−8·7
Ammonium chloride	25·0	−15·4

If snow is available, lower temperatures are obtainable, as will be seen from the following table :—

Substances used per 100 parts of Snow.	Freezing Point. °C.
13·5 parts potassium nitrate and 26 parts ammonium chloride	−17·8
33 parts sodium chloride	−21·3
52 parts ammonium nitrate and 55 parts sodium nitrate	−25·8
9 parts potassium nitrate and 67 parts ammonium rhodanate	−28·2
13 parts ammonium chloride and 37·5 parts sodium nitrate	−30·7
32 parts potassium nitrate and 59 parts ammonium rhodanate	−30·6
2 parts potassium nitrate and 112 parts potassium rhodanate	−34·1
39·5 parts ammonium rhodanate and 54·5 parts sodium rhodanate	−37·4
143 parts crystallised calcium chloride ($CaCl_2 + 2H_2O$)	−50·0

The freezing point of fatty oils is not characteristic enough for purposes of classification or identification. The determination of it is therefore resorted to in exceptional cases only, as in the

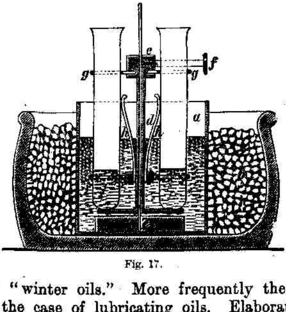


Fig. 17.

examination of "winter oils." More frequently the determination is required in the case of lubricating oils. Elaborate methods for testing lubricating oils have been worked out by the officials of the Königliche Technische Versuchsanstalten, Berlin. Fig. 17 illustrates

[1] *Journ. Soc. Chem. Ind.* 1889, 423.

the apparatus in which the determination is carried out. (Cp. "Cold-Test," chap. xv.).

3. Refractive Power

The ease and rapidity with which the refractive index can be determined, in consequence of the recent improvements in optical apparatus, has given prominence to the refractometric method of examining oils and fats. Although this method does not afford a perfectly reliable means of detecting adulteration, still in many cases it can be used as a kind of sorting test, allowing us to rapidly establish whether adulteration may be suspected, or whether a genuine sample

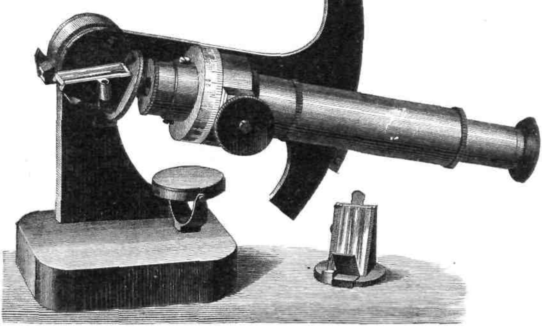


Fig. 18.

is under examination. The objection of earlier observers as to the great influence on the refractive index of the methods of refining, the age of the oil, the amount of free fatty acids, the amount of oxidation the oil has undergone, have been shown to be, to a large extent, unfounded, and recent researches have proved that very valuable indications, especially in the case of butter fat, can be gained from the determination of the refractive index.

In *Abbe's* refractometer the index of refraction is found by observing the total reflection which a very thin stratum of a liquid placed between prisms of a more highly refracting substance produces in transmitted light.[1] A single drop of any fluid is therefore sufficient for the examination, however opaque that fluid may be in a thick layer.

[1] E. Abbe, *Neue Apparate zur Bestimmung des Brechungs- und Zerstreuungs-vermögens fester und flüssiger Körper.* Jena, 1874.

The instrument[1] is shown in Figs. 18 and 19. The former illustrates the position in which the drop of the fat under examination is applied; the latter shows that position of the instrument in which the readings are taken. The instrument consists of a double prism of a highly refracting flint glass (Fig. 18) fixed to an alhidade

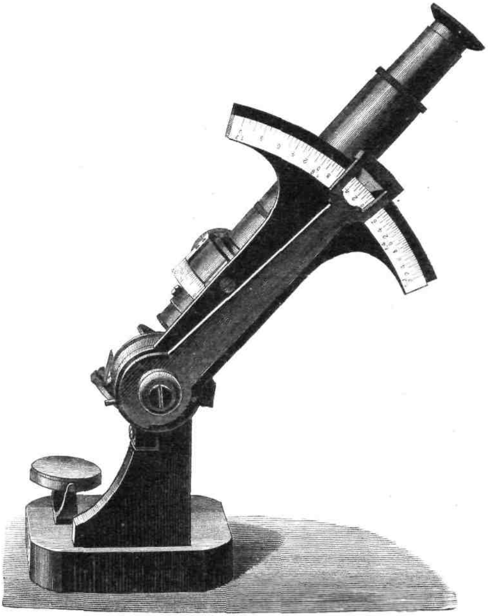


Fig. 19.

in such a way that both admit of being turned round the centre of a divided arc. This arc has fastened to it a telescope turning with it on a horizontal pin. The elongated part of the telescope fits in a support carrying a system of two revolving *Amici* prisms. This system acts as a compensator for achromatising the critical line of total reflection, the amount of rotation being indicated by a divided

[1] Made by Carl Zeiss, Optische Werkstätte, Jena.

drum. The drop of liquid to be examined is brought between the two prisms, one of which can be removed easily as shown. In order to make this prism easily accessible, the telescope with the arc may be turned down.

The examination may be made with diffused daylight or lamp-light, and consists in a single adjustment of the alhidade. The refractive index is read directly off the divided arc to the third decimal, no calculation being necessary. The fourth decimal may be estimated accurately within two units.

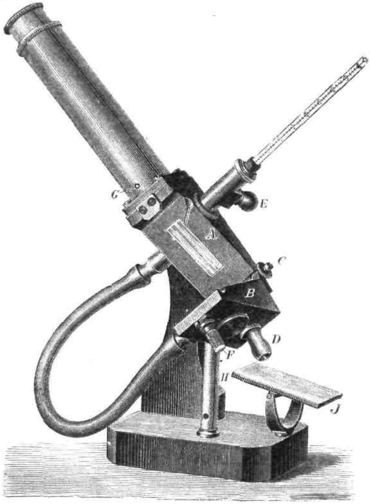


Fig. 20.

Since for the examination of butters *Zeiss's* butyro-refractometer (Fig. 20) has been introduced, the butyro-refractometer has almost completely superseded *Abbe's* refractometer. Only in those cases where the refractive indices of the oils lie outside the range of the butyro-refractometer, as in the case of tung oil and rosin oils, the *Abbe* refractometer is required. The butyro-refractometer differs from the *Abbe* instrument in that the critical line of total reflection for a certain substance—in this case butter fat—is achromatised, not by a special compensating arrangement, but by the refractometer prisms themselves, the dispersion co-existent with the total reflection between

glass and substance being exactly compensated by the dispersion due to the surface when the light emerges from the double prism in the direction of the telescope. Accordingly, the critical line appears colourless (achromatised) for the standard substance for which the prisms have been calculated, whilst all substances differing from it in refractive and dispersive power cause the critical line to appear more or less blue when the dispersion is higher, or red when it is lower than that of the standard substance. The critical line is, however, in all cases sufficiently distinct to admit of its exact position being ascertained. Thus two different substances are, in the first instance, distinguished by the different positions of the critical line, and next by the difference in its appearance as regards a coloured fringe. Since the prisms of the butyro-refractometer are specially calculated for pure butter fat, the presence of foreign fats in a sample of butter fat may be easily detected by a simple examination under this instrument.

To make an observation, place the instrument upon a table, where diffuse daylight or any form of artificial light can be readily admitted for illumination. Supply through nozzle D a stream of water of a constant temperature.[1] Then open the prism casing by giving to pin F about half a turn to the right, until it meets with a stop, and turn the half B (held in position by H) of the casing aside. The prism surfaces must now be cleaned with the greatest care; this is best done by applying soft linen moistened with a little alcohol or ether. Then pour a few drops of the clear (filtered) fat on the surface of the prism contained in casing B. For this purpose the apparatus should be raised with the left hand, so as to place the prism surface in a horizontal position. Then press B against A, and bring F back into its original position by turning it in the opposite direction.

While looking into the telescope, give the mirror J such a position as to render the critical line which separates the bright left part of the field from the dark right part distinctly visible. If the space between the prisms is not filled completely with the sample, the critical line will not appear distinct. Finally adjust the movable part of the telescope, so that the scale becomes clearly visible.

The critical line, somewhat hazy at first, approaches after a short time a fixed position and quickly attains its greatest distinctness. This point being reached, the reading of the thermometer is taken, unless a definite temperature has been arranged for at the outset. The adjustment of the instrument should be tested periodically by means of a *standard fluid* (supplied with the instrument), the critical line of which must occupy a definite position on the scale. By the aid of a watch-key inserted in G, the position of the objective can be altered at will.

The scale divisions may be converted into refractive indices by reference to the following table:—

[1] Cp. Figs. 24 and 25, p. 190.

Table of Refractive Indices

Scale Division.	D.	Difference.
0	1·4220	
10	1·4300	8·0
20	1·4377	7·7
30	1·4452	7·5
40	1·4524	7·2
50	1·4593	6·9
60	1·4659	6·6
70	1·4723	6·4
80	1·4783	6·0
90	1·4840	5·7
100	1·4895	5·5

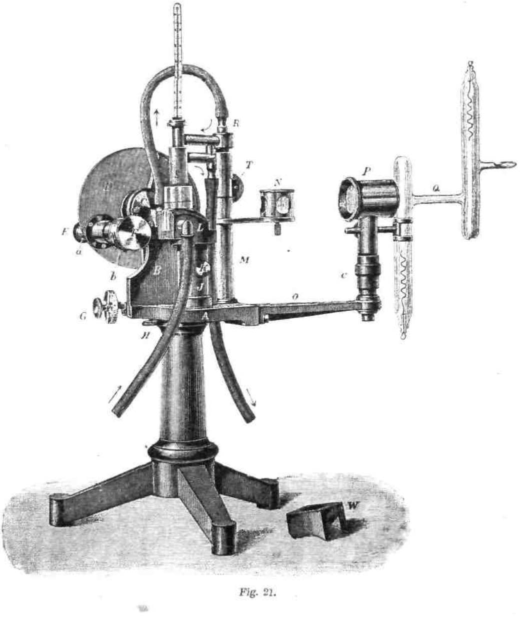


Fig. 21.

Pulfrich's[1] refractometer is also provided with a special arrangement for observations at somewhat elevated temperatures. This refractometer[2] is shown in Fig. 21. The observations are made with sodium light, placed opposite the reflecting prism N, or with hydrogen light, emanating from the Geissler tube Q. The sodium light is thrown by means of the reflecting prism N, and the hydrogen light by means of the condenser P, on to the substance under examination. (The illumination can be changed rapidly from one source of light to the other by displacing N.) The substance is

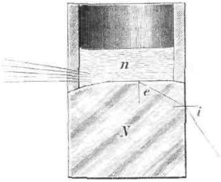


Fig. 22.

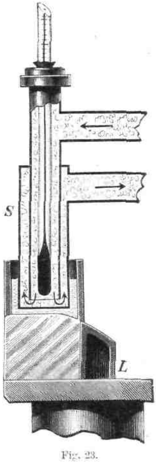


Fig. 23.

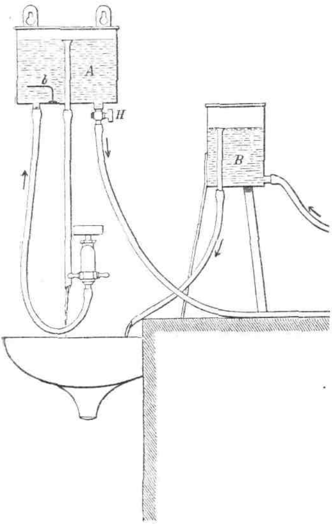
placed direct on to the surface of the refractometer prism in the manner illustrated by Fig. 20, and the prism, together with the substance, can be brought to any desired temperature in a special heating apparatus S (Fig. 23), by allowing the heating liquid to flow in the direction indicated by the arrows. The piece of wood *W* (Fig. 21) serves to prevent loss of heat.

The light falling into the substance to be examined under grazing incidence passes through the vertical face of the 90° prism, and the angle *i* at which the limiting ray emerges from the vertical face is read off by means of a telescope and graduated circle. The refractive

[1] C. Pulfrich, *Das Totalreflectometer und das Refractometer für Chemiker*, etc. Leipzig, 1890.
[2] Made by Carl Zeiss, Optische Werkstätte, Jena.

index n of the substance is calculated by means of the formula $n = \sqrt{N^2 - \sin^2 i}$, where N is the (known) refractive index of the prism.

For the convenient supply of wâter at a constant temperature and under constant pressure to the butyro-refractometer, a water-pressure regulator (Fig. 24), consisting of the two vessels A and



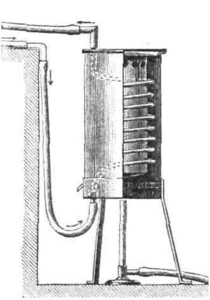


Fig. 25.

Fig. 24.

B, may be used in conjunction with a thermostat[1] (Fig. 25). The butyro-refractometer is inserted between the thermostat and vessel B.

A combination of the *Abbe* refractometer with the heating apparatus of the butyro-refractometer—necessary for the determination of the refractive indices of such oils as tung oil and rosin oil (see p. 186) at a constant temperature—is shown in Fig. 26.

Another instrument based on an arbitrary scale has been recom-

[1] A somewhat more convenient thermostat, occupying less space, has been recently recommended by T. E. Thorpe, *Journ. Chem. Soc.* 1904, 257.

mended by *Amagat* and *Jean* for the examination of oils and fats, and especially for testing butter. The apparatus, named by its designers oleo-refractometer (Fig. 27), consists essentially of a collimator, a telescope, and a metallic vessel. The latter is fitted with parallel plate-glass sides, and its position to the collimator and telescope is fixed in such a way that a ray of light entering through the collimator must pass through the plate-glass sides and the telescope. In the centre of the metallic vessel a small hollow silver

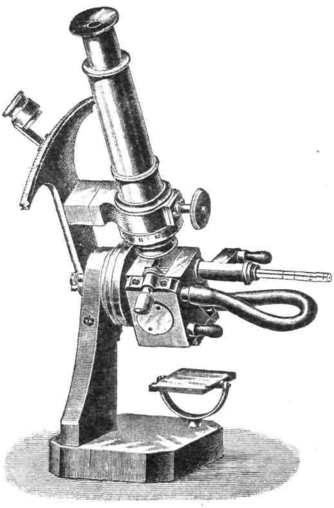


Fig. 26.

cylinder A with two plate-glass ends is inserted, arranged so as to form an angle of 107°. The telescope is furnished with an arbitrary glass scale, H, placed in the focus of the eye-piece, M, on which is thrown the image produced by a semicircular stop inserted in the collimator, thus dividing the field into a dark and light portion. Suppose the silver cylinder and the outer circular vessel be filled with the same oil, there will be no refraction, and consequently no alteration in the position of the image. If, however, the inner silver cylinder be filled with a different oil, there will be refraction depending on the nature of the oil, and consequently the line dividing the field will be

displaced to the right or left. The amount of displacement is read off the scale of the telescope, and is expressed by the number of scale divisions or "degrees."

For practical use the outer vessel is filled with a standard oil (*huile type*) [the composition of which is, curiously enough, kept secret by the inventors;[1] it is supplied together with the instrument], and the semicircular stop so adjusted that the line dividing the field

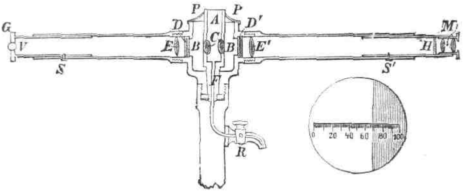


Fig. 27.

into a dark and light portion falls on the zero point of the scale. The inner cylinder is then filled with the oil under examination, and the displacement of the dividing line, *i.e.* the amount of refraction, read off. Instead of using the "standard oil" one may, of course, compare a sample of oil with a sample of the same kind known to be pure.

For the sake of greater convenience in practical use both the cylindrical vessel and the silver cylinder can be emptied (and washed out) by means of taps, one of which only, R, is shown in Fig. 20. Besides, a water-jacket surrounding the centre part of the instrument (not shown) allows the temperature of the oil under examination to be regulated. The water in the jacket can be heated by means of a lamp to any desired temperature, which is read off a thermometer.

Amagat and *Jean's* oleo-refractometer has this advantage over the refractometers described above that, being a differential apparatus, it allows of a rapid determination of the difference of two oils which are compared under exactly the same conditions.[2] Another instrument for the refractometric examination of oils has been constructed by *Féry*.

The refractive constant varies in inverse ratio to the temperature, hence it is necessary that observations should be made at a constant temperature. *Tolman* and *Munson*[3] have calculated from observations made by *Procter*[4] on a number of oils the correction 0·000365 for each degree Centigrade. In the butyro-refractometer the correction

[1] The "huile type" is sheep's foot oil.

[2] Allen (*Analyst*, 1895, 135) points out that the angle of the prism is not strictly the same in all instruments, he having found for a sample of lard in three instruments $4\frac{1}{2}°$, 6°, and 11° respectively.

[3] *Journ. Amer. Chem. Soc.* 1902, 754. [4] *Journ. Soc. Chem. Ind.* 1898, 1023.

for butter fat is 0·55 scale divisions ("degrees") for each degree Centigrade; but this correction would not be applicable to other oils and fats. In order to avoid complications, it is best to make all observations at a definite temperature, to be agreed upon. It is advisable to adopt 40° C. as the standard temperature. Most oils and fats are liquid at 40° C., and only in exceptional cases, such as beeswax, a higher temperature will be required. But whatever temperature be chosen, the temperature must be distinctly stated.

The presence of free fatty acids in oils and fats appears to affect the refractive index to a marked degree. Thus a sample of Californian olive oil,[1] containing 44·4 per cent of free fatty acids, had the refractive index 1·4672, whereas the corresponding value for a large number of less acid samples was 1·4711.

The following table contains a number of values, obtained by means of an *Abbe* refractometer, the oleo-refractometer, and the butyro-refractometer respectively, which I have arranged, following the system of classification adopted in this work, in the order of the iodine values of the oils, fats, and waxes, so that it may be seen at a glance whether a correlation can be established between the iodine number and refractive power. No definite relation, however, can be established. It is remarkable that the oils belonging to the class "Terrestrial Animal Oils" deviate to the left in the oleo-refractometer, and it would appear as if terrestrial animal oils could be readily differentiated from vegetable oils by their behaviour in the oleo-refractometer.

Oil.	*Class.*	*Group.*	Refractive Index.					
					Oleo-refractometer.		Butyro-refractometer.	
			°C.		°C.	Degrees.	°C.	Degrees.
Linseed	Drying oils		15 60	1·4835 1·4660	22 ...	+50 to +54 ...	20 40	84-90 72·5
Tung			19	1·503	22	+75		
Candle nut			...	...	...	...	15 20	76 78·5
Stillingia			...	...	...	...	35	75
Hemp seed			...	...	22	+34 to +37		
Walnut, nut			...	1·4804	22	+35 to +36	40	64·8
Safflower			...	...	...	...	40	65·2
Poppy seed			60	1·4586	22	+30 to +35	40	63·4
Asparagus seed			...	...	...	...	25	75
Amoora			...	...	...	...	40	64·5
Niger seed			...	...	22	+26 to +30	40	63·0
Sunflower			60	1·4611	22	+35	25	72·2
Argemone			...	...	...	...	40	62·5

[1] Tolman and Munson, *Journ. Amer. Chem. Soc.* 1903, 955.

Oil.	Class.	Group.	Refractive Index.					
					Oleo-refractometer.		Butyro-refractometer.	
			°C.		°C.	Degrees.	°C.	Degrees.
Cameline . . .	Semi-drying oils	Cotton seed oil group	...	...	22	+32		
Pumpkin seed . .			...	...	...	...	25	70·2-72
Maize (corn) . .			15 20	1·47665 1·47625				
Wheat . . .			20	1·48325	...	...	...	74·5
Beech nut . .			...	...	22	16·5 to 18		
Kapok . . .			...	...	...	...	40	51·3
Cotton seed . .			15	1·4743-1·4752	22	+17 to +23	25 40	67·6-69 58·0
Sesamé . . .			15	1·4748-1·4762	22	+13 to +17	25	68
Croton . . .			...	...	22	+35	27	77·5
Curcas, purging nut .			25	1·4681-1·4687	...	...	25 40	65 56·5
Garden cress . .		Rape oil group	...	...	...	...	40	60·5
Ravison . . .			...	...	22	+18 to +25	20	73-74
Hedge mustard .			...	...	...	...	25	70·5-71
Rape (colza) . .			15	1·4720-1·4757	22	+16 to +20	25	68
Black mustard . .			...	...	...	...	40	59·5
White mustard .			...	...	...	...	40	58·5
Radish seed . .			...	...	...	...	40	57·5
Small fennel . .	Non-drying oils		...	...	...	...	40	58·5
Quince . . .			...	1·4729				
Apricot kernel . .			...	...	...	...	25	66·6
Peach kernel . .			...	...	22	+7·5 to +11·5	25	66·1-67
Almond . . .			60	1·4555	22	+8 to +10·5	25	64·4
Wheat meal . .			25	1·4851	...	...	25	92
Acorn . . .			...	1·4731				
Californian nutmeg .			...	1·4766				
Arachis . . .			60	1·4545	22	+4 to +7	25	66-67·5
Tea seed . . .				...	22	+8		
Elderberry . .			20	1·472				
Olive . . .			15	1·4698-1·4716	22	0 to +3·5	25 40	62·4 53·5-54
Olive kernel . .			25	1·4682				
Coffee berry . .			25	1·4777	...	...	25	79
Ben			...	...	...	...	40	59
Paradise nut . .			...	...	...	...	15	61·4
Castor . . .		Castor oil group	15	1·4799	22	+39 to +42	25	78
Pilchard . . .	Marine animal oils	Fish oils	...	...	...	+32 to +36		
Japan fish . .			...	...	22	+50 to +53		

Oil or Fat.	Class.	Group.	Refractive Index.					
					Oleo-refractometer.		Butyro-refractometer.	
			°C.		°C.	Degrees.	°C.	Degrees.
od liver . . .	Marine animal oils	Liver oils	15	1·4800-1·4852	22	+40 to +48	25	75
hark liver .			...	...	22	+29 to +35		
eal		Blubber oils	...	...	22	+30 to +36		
Vhale . . .			...	...	22	+42 to +48	25	70
heep's foot . .	Terrestrial animal oils		...	...	22	0		
Iorse's foot . .			...	...	...	−6 to −12		
Ieat's foot . .			...	...	22	−1 to −3		
gg			25	1·4713	...	...	25	68·5
allow oil . .			...	...	...	−1 to −5		
ard oil . . .			...	...	...	0 to +1·0		
ongam oil . .	Vegetable fats		...	...	...	...	40	70-78
Iargosa oil . .			...	...	...	...	40	52
Iahua butter . .			...	...	...	...	40	52·1
alm oil . . .			60	1·4510				
egetable tallow .			...	...	...	−23		
utmeg butter .			40	1·4704	...	...	40	48-85
hulwara butter .			...	...	...	...	40	48·2
acao butter . .			60	1·4496	...	...	40	46-47·8
okum butter . .			25	1·4628	...	...	25	1·4628
alm nut oil . .		Cocoa nut oil group	60	1·4431	...	...	40	36·5
ocoa nut oil . .			60	1·4410	45	−59	40	+34
Iare	Animal fats	Semi-drying fats	...	...	...	...	40	49
abbit (tame) . .			...	...	...	...	40	49
Iorse . . .			...	...	...	...	40	53·7
oose (domestic) .		Non-drying fats	...	...	...	...	40	50-50·5
uman (adult) .			...	...	...	...	40	49·6-53·1
ard . . .			60	1·4539	22	−12·5	40	48·6-51·2
eef tallow . .			60	1·4510	...	...	40	49
utton tallow . .			60	1·4510				
utter . .			60	1·448-1·445	45	−25 to −31	40	41-42
tag . . .			...	...	...	...	40	44·5
perm oil . .	Liquid waxes		...	...	22	−12 to −17·5	40	46·2
rctic sperm oil .			...	...	22	−13		
eeswax . . .	Solid waxes	Animal waxes	...	...	...	...	62	29·5-30

The following table gives some observations on mixed fatty acids in *Abbe's* refractometer,[1] collated with the numbers observed on the oils and fats themselves. I have also added a few isolated observations of butyro-refractometer values of liquid fatty acids (*Bömer*).

Refractive Indices of Fatty Acids

Kind of Oil.	Refractive Index at 60° C.		Butyro-refractometer "Degrees" at 40° C.
	of the Oil.	of Mixed Fatty Acids.	of Liquid Fatty Acids.
Linseed	1·4660	1·4546	
Poppy seed	1·4586	1·4506	
Sunflower	1·4611	1·4531	
Cotton seed	1·4570	1·4460	51·4-54·7
Sesamé	1·4561	1·4461	
Rape (crude)	1·4667	1·4491	
Castor	1·4636	1·4546	
Almond	1·4555	1·4461	
Arachis	1·4545	1·4461	
Olive	1·4548	1·4410	42·7
Cod liver oil	1·4621	1·4521	
Palm oil	1·4510	1·4441	
Cacao butter	*1·4496*	*1·4420*	
Palm nut oil	1·4431	1·4310	
Cocoa nut oil	1·4431	1·4295	
Lard	1·4410	1·4395	
,, (European)	...	...	42·8-44·2
,, (American)	...	...	43·1-44·7
Tallow (Beef)	1·4539	1·4375	
,, (Mutton)	1·4510	1·4374	
Butter	1·445-1·448	1·437-1·439	
Margarine	1·443-1·453	1·443-1·444	

The influence of heating on the refractive index has been studied by *Utz*. His results are reproduced in the following table :—

	Original Oil and Fat.		Heated One Hour in Water Oven.		Heated Three Hours in Water Oven.		Heated Ten Hours in Water Oven.		Heated Two Hours at 145° C.	
	Refractive Index.	Butyro-refractometer.	Refractive Index.	Butyro-refractometer.	Refractive Index.	Butyro-refractometer.	Refractive Index.	Butyro-refractometer.	Refractive Index.	Butyro-refractometer.
Refraction at 20° C.										
Cotton seed oil	1·4780	79·4	1·4780	79·4	1·4799	82·7	1·4813	85·2	1·4825	87·3
Cod liver oil	1·4778	79·1	1·4776	78·7	1·4804	83·6	1·4805	83·8	1·4823	86·9
Olive oil	1·4688	64·5	1·4689	64·7	1·4696	65·7	1·4696	65·7	1·4698	66·1
Sesamé oil	1·4730	71·1	1·4730	71·1	1·4731	71·3	1·4732	71·4	1·4738	72·4
Refraction at 40° C.										
Butter fat (fresh)	1·4536	41·7	1·4535	41·5	1·4538	42·0	1·4539	42·1	1·4546	43·4
,, (old)	1·4533	41·3	1·4534	41·4	1·4540	42·3	1·4549	43·6	1·4554	44·3
Cacao butter	1·4537	41·8	1·4535	41·5	1·4570	46·6	1·4574	47·2	1·4583	48·5
Cocoa nut oil	1·4497	36·3	1·4498	36·4	1·4493	35·7	1·4500	36·7	1·4505	37·4
Lard	1·4606	51·9	1·4606	51·9	1·4605	51·7	1·4617	53·6	1·4625	54·8
Tallow (Beef)	1·4551	43·9	1·4550	43·7	1·4570	46·6	1·4580	48·0	1·4586	48·9
,, (Mutton)	1·4550	43·7	1·4550	43·7	1·4568	46·3	1·4582	48·3	1·4588	49·2

[1] Thoerner, *Journ. Soc. Chem. Ind.* 1895, 43.

Procter[1] proposed to determine the specific refraction of oils and fats, but since hitherto little practical use attaches to this constant, the reader must be referred to the original paper.

4. Viscosity

Viscosity may be defined as the resistance the smallest particles offer to their sliding past one another, in other words, viscosity is the internal friction of the oil. This internal friction by no means bears any known relation to the density of the liquids. A useful determination of the viscosity is based on *Poiseuille's* law[2] of the flow of the liquid through a capillary tube. This law is expressed by the following formula :—

$$\mu_1 = \frac{\pi p r^2}{8vl} \cdot t$$

where μ_1 is the coëfficient of the internal friction or viscosity ;
- p the pressure on the unit surface of the orifice of the capillary tube ;
- r the radius of the tube ;
- l the length of the tube ;
- v the volume of liquid that has passed through the apparatus in t seconds.

This law holds good only if the capillary is as long as $\frac{l}{2r}$.

For practical purposes it would be too tedious to use apparatus having capillary efflux tubes ; hence, for the commercial examination of oils, the diameter of the efflux tube is usually taken somewhat large, and the height of the column of the liquid somewhat small.

The viscosity is usually determined by ascertaining the times two equal volumes of the liquids under comparison take to flow through a narrow aperture under exactly the same conditions.

For a rough comparison, it may suffice to use a wide glass tube drawn out to a narrow aperture of about 2 mm., at the lower end, and having an upper and lower mark for the exact measurement of the volume of liquid.

In the earliest experiments which were carried out by *Schübler*, a glass tube of 2 cm. diameter and 10 cm. height, having attached to it a narrow tube of 1·6 mm. diameter, was employed. They are given in the following table :—

[1] *Journ. Soc. Chem. Ind.* 1898, 1023. *Cp.* Lewkowitsch, *Ibid.* 1898, 1025.

[2] With regard to the determination of the absolute viscosity, cp. chap. xv., "Lubricating Oils—Lubricants."

Name of Oil.	Number of Seconds required at		Viscosity at	
	+15° R.	+7·5° R.	+15° R.	+7·5° R.
Castor oil . . .	1830	3390	203·3	377·0
Olive oil . . .	195	284	21·6	31·5
Colza oil . . .	162	222	18·0	22·4
Winter rape oil . .	159	204	17·6	22·6
Beechnut oil . .	158	237	17·5	26·3
White mustard oil .	157	216	17·4	24·0
Almond oil . .	150	209	16·6	23·3
Summer rape oil .	148	205	16·4	22·7
Rape oil . . .	142	200	15·8	22·2
Mustard seed oil .	141	175	15·6	19·4
Summer rubsen oil .	136	198	15·1	22·0
Poppy seed oil . .	123	165	13·6	18·3
Cameline oil . .	119	160	13·2	17·7
Sunflower oil . .	114	148	12·6	16·4
Peach kernel oil .	93	132	10·3	14·7
Walnut oil . .	88	106	9·7	11·8
Linseed oil . .	88	104	9·7	11·5
Hemp seed oil . .	87	107	9·6	11·9
Distilled water . .	9	9	1·0	1·0

On dividing the number of seconds required for an oil—e.g. 1830 —by that required for water at the same temperature—*e.g.* 9—a number is obtained which is termed *specific viscosity*, or in short, *viscosity*. Thus the viscosity of castor oil, according to *Schübler*, would be $\frac{1830}{9} = 203{\cdot}3$ at 15° C.

In practice the viscosity of oils is frequently compared with that of rape oil. *Redwood*[1] found from a number of tests carried out with refined rape oil in his viscosimeter, that 535 seconds may be considered as the average number occupied by the outflow of 50 c.c. of refined rape oil at 60° F. (15·5° C.), the viscosity of water being under similar conditions 25·5.

Taking rape oil as a standard, and putting its viscosity = 100, the viscosity of any other oil under examination would then be found by multiplying the number of seconds occupied by the outflow of 50 c.c. by 100, and dividing by 535. In case of the oil having a different specific gravity from that of rape oil—0·915 at 60° F.—*Redwood* introduces a correction by multiplying the result by the specific gravity of the sample, and dividing by 915. Therefore, if n be the number of seconds for an oil under examination, and s its specific gravity, the following formula would be arrived at:—

$$\text{Viscosity} = \frac{n \times 100 \times s}{535 \times 915} = \frac{n \times 100 \times s}{489{,}525}.$$

Since, however, there is no correlation between specific gravity

[1] *Journ. Soc. Chem. Ind.* 1886, 127.

and viscosity (see above), I consider it more useful to record the numbers as obtained by direct determination of the viscosity.

Engler uses water as a standard liquid, 200 c.c. taking 53 seconds at 20° C. to flow through his apparatus. If n be the number of seconds required by an oil under the same conditions, the quotient $\frac{n}{53}$ will represent the specific viscosity of the oil.

In order to obtain comparable results, complete uniformity of construction in apparatus is essential. Passing over a number of forms of apparatus that have been proposed from time to time,[1] I shall describe only three—those of *Redwood*, *Saybolt*, and *Engler*. The first apparatus has been adopted by the War Department, the principal Railway Companies, and the Scottish Mineral Oil Association; the second is largely used in the United States; and the third occupies, in Germany, a similar position to that of *Redwood's* in this country.

Redwood's viscosimeter[2] (Fig. 28) consists of a silvered copper oil-cylinder C, about $1\frac{7}{8}$ in. in diameter, by about $3\frac{1}{2}$ in. in depth. The bottom of this cylinder is provided with an agate jet D, the cup-shaped cavity of which can be closed by means of the plug E, consisting of a small silvered brass sphere attached to a wire. Inside the oil cup and at a short distance from the top there is fixed a small bracket F, terminating in a point. This serves as a gauge of the height to which the oil must be filled. A thermometer T is usually immersed in the oil and supported by means of a clip holding the plug E. The cylinder C is surrounded with a copper jacket J, having a closed side tube K, by means of which the liquid in the jacket can be brought to any desired temperature. The heated liquid rising from K is uniformly distributed through the bath by means of a revolving agitator worked by the handle H. The temperature of the liquid is controlled by the thermometer T′. The whole instrument is supported on a tripod stand provided with levelling screws.

It is of the greatest importance that the orifice in the agate jet should be of a standard size, as slight variations in the size of the hole in different instruments are apt to lead to discordant results.

The viscosimeter observation is made in the following manner:— The copper jacket is filled with water for temperatures up to about 95° C., and for higher temperatures with a suitable mineral oil, up to a height corresponding roughly with the pointer F in the cylinder C. After the liquid in the bath has been heated to the required temperature, the oil to be tested, previously purified and dried, and brought

[1] Dollfus, *Dingl. Polyt. Journ.* 153, 231; Vogel, *ibid.* 168, 267; Fischer, *ibid.* 236, 487; Lamansky, *ibid.* 248. 29. Lamansky's viscosimeter has been improved in the Nobel refineries at Baku, cp. *Chem. Rev. über Fett u. Harz Industrie*, 1897, 90. Lepenau; *Zeitsch. f. analyt. Chemie*, 24, 465. See also Redwood, *Journ. Soc. Chem. Ind.* 1886, 121, Mills, *ibid.* 1886, 148; Hurst, *ibid.* 1892, 418; Neumann-Wender, *ibid.* 1895, 596; Killing, *ibid.*; Redwood, *Petroleum*, 1896, vol. ii. pp. 602-620. Meggitt, *Journ. Soc. Chem. Ind.* 1902, 106. Coleman-Archbutt's viscosimeter is described on p. 140 of Archbutt and Deeley's *Lubrication and Lubricants.*

[2] *Journ. Soc. Chem. Ind.* 1886, 126.

to the same temperature, is poured into C until its level just coincides with the point of the gauge. Great care must be taken that this level be reached exactly, and that the temperature remain constant

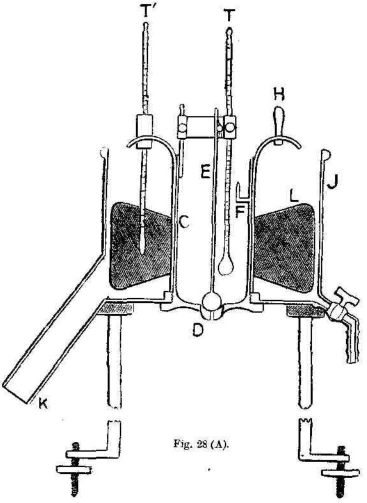


Fig. 28 (A).

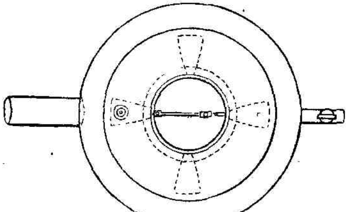


Fig. 28 (B).

during the observation. A narrow-necked flask, holding 50 c.c. to a point marked on the neck, is then placed beneath the jet in a vessel containing a liquid of the same temperature as the oil. The plug is

then raised, and the number of seconds required for 50 c.c. of the oil to flow out is carefully observed by means of a chronometer. At least two tests should be made at the same temperature; the two results should be very closely concordant if due care has been exercised.

Allen[1] has modified *Redwood's* viscosimeter with a view to maintaining a given head of oil throughout the experiment. For this purpose the top of the *oil-cylinder (Fig. 29)* is fitted with an air-tight cap perforated by two holes, one of which is furnished with a tap B, while into the other a tube is screwed air-tight. This tube C is prolonged on two sides till it is in contact with the agate orifice, while the angles of the inverted V-shaped slits, cut on each side, terminate at a definite height D above the orifice. The cylinder is completely filled with oil before commencing an experiment, the tap B is closed, and the orifice opened till the oil sinks in the inner tube to the level D. Air then bubbles in regularly at D, and rises into the closed space above the oil, and when this is observed to happen, the oil is collected in a graduated cylinder. When using this apparatus, there is no necessity to collect exactly 50 c.c., because the oil runs through at a constant rate.

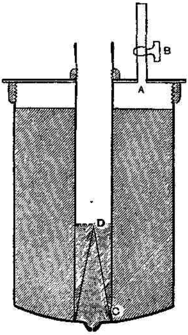


Fig. 29.

The same principle has been adopted by *E. Schmid*[2] in the improved *Reischauer* viscosimeter (see Fig. 30).

Saybolt's viscosimeter.[3] The oil vessel of this viscosimeter is placed in a water-bath of considerable capacity. The jet of the viscosimeter is of metal, and is enclosed in a tube extending below the orifice. The oil vessel is contracted, as shown (Fig. 31), above the jet, and is cut away longitudinally on each side, to expose a glass tube which lines it. Glass windows are provided in the water-bath. The upper edge of the oil vessel is fitted with an oil-tight gallery having a raised edge, and communicating with the oil vessel, which extends to the same level as the top of the gallery, by a number of small holes. In using the apparatus, the water-bath is filled with water of the required temperature, and a cork having been inserted in the mouth of the tube enclosing the jet, the oil vessel is filled with the sample to be tested, until it overflows through the holes into the gallery. The oil is then stirred with a thermometer, and the temperature adjusted if necessary. On withdrawing the thermometer, the oil which it had displaced flows back from the gallery; the latter is then emptied

[1] *Journ. Soc. Chem. Ind.* 1886, 131. [2] *Chem. Ztg.* 1885, 1514.
[3] The description of this viscosimeter is taken from Redwood, *Petroleum*, vol. ii. p. 608.

by means of a pipette. The length of the oil column is, of course, determined by the position of the holes connecting the oil vessel with the gallery. The flow of oil from the jet is started by withdrawing the cork, and a stop-watch is set in motion. The watch is stopped

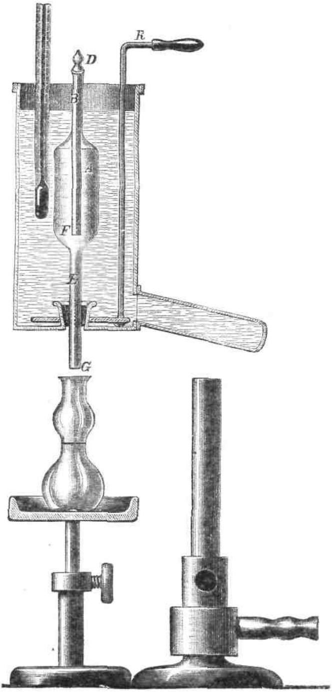


Fig. 30.

when the operator sees the surface of the oil through the glass tube above mentioned.

Engler's viscosimeter[1] in its latest form, as designed by him in conjunction with the officials of the Charlottenburg Mechanisch-

[1] *Journ. Soc. Chem. Ind.* 1893, 292.

Technische Versuchsanstalt, is shown in Fig. 32. The oil vessel, A is made of sheet brass, the inside of which should be gold-plated for very accurate determinations. This vessel is closed by a cover, A′, perforated by two holes, into one of which the thermometer *t* is fitted, whilst the other serves to receive the plug *b*. The delivery tube *a* projecting from the convex bottom of the vessel A must be exactly 20 mm. long, and 2·9 mm. in diameter at the top and 2·8 mm. at the bottom. The *delivery tube should* preferably be made of platinum, as in course of time even brass is attacked by neutral oils. The plug *b* should be made of hard wood. Three pointers *c* serve the double purpose of indicating

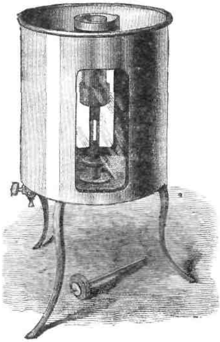


Fig. 31.

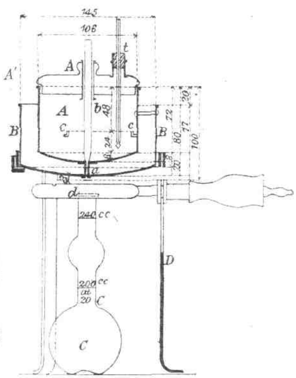


Fig. 32.

the correct level of the apparatus and of marking the exact volume of 240 c.c. The vessel A is jacketed, vessel B serving as a receiver for mineral oil, which may be heated up to 150° C. by means of gas supplied through tube *d*. As shown in the figure, this jacket also surrounds the delivery tube *a*, thus preventing loss of heat whilst the oil flows out. The instrument is fastened on to the tripod D. Beneath the apparatus is placed a flask C bearing two marks on the neck for 200 c.c. and 240 c.c. respectively.

Engler lays the greatest possible stress on the necessity of strictly adhering to the measures given in Fig. 32, if correct results are to be obtained.[1]

[1] "The normal apparatus" is manufactured under the joint control of the Charlottenburg Technische Anstalt and the Karlsruhe Chemisch-Technische Versuchsanstalt, and may be also had from *C. Desaga* of Heidelberg. Apparatuses from other sources are according to *Engler* not made with the requisite care, and give discordant results.

In order to test the instrument, the time taken by the outflow of 200 c.c. of water at the temperature of 20° C. must be determined first. Clean vessel A with ether or petroleum ether, and rinse out with alcohol and water. Wipe out tube *a* by means of a feather or filtering paper, and close it with the plug *b*. Measure off, by means of the flask, C, 240 c.c. of water, and pour it into vessel A. This should then be filled exactly up to the level of the pointers *c*. Heat the mineral oil in B, if necessary, to 20° C., and wait until the water in A has attained the same temperature. In the meantime dry flask C and place it under the delivery tube *a*. Draw the plug and carefully note the time (by means of a chronometer) required to fill the flask C up to the 200 c.c. mark. It is most important that the water in A should be completely at rest before the plug is drawn. The time required should be from 51 to 53 seconds for a correct instrument, and repeated observation should not differ by more than 0·5 of a second.

Before an oil is examined, every trace of dirt and moisture must be removed from A by wiping it out carefully and rinsing it successively with alcohol and ether (or petroleum ether); finally it should be rinsed out with the filtered and dried oil. The oil is then poured into A up to the pointers *c*, and heated to the desired temperature, at which it must be kept for at least two or three minutes before allowing it to run out.

The following table gives a comparison of results based on a number of experiments with the three viscosimeters:[1]—

Viscosimeter.	Seconds for outflow of	
	50 c.c. at 70° F.	200 c.c. at 20° C.
Redwood's . .	100	—
Saybolt's . .	56	—
Engler's . .	—	170

As will be seen, *Engler's* viscosimeter requires much more time than either of the other two viscosimeters, and it has been proposed to shorten the observation by taking the number of seconds after 50 c.c. or 100 c.c. have run out, and multiplying the number of seconds by empirically found constants.[2] Surely, it would be simpler to use an apparatus based on the outflow of 50 c.c., like *Redwood's!*

As a rule, the viscosity of an oil destined to serve as a lubricant is determined at a temperature approximating to that at which the oil is actually used. Since *Engler's* viscosimeter has not been found

[1] Redwood, *Petroleum*, vol. ii. p. 610.

[2] Singer, *Chem. Rev. über die Fett u. Harz Industrie*, 1897, 93, shows that the constants 5 for 50 c.c., and 2·34 for 100 c.c., give results agreeing with those found by allowing 200 c.c. to run out.

suitable for observations at higher temperatures, *Engler* and *Künkler*[1] designed a "viscosimeter for examination of oils under constant temperature." This instrument is represented by Fig. 33. It is an octagonal jacketed air-bath made of sheet brass, 35 cm. high and 20 cm. wide. The feet *a* stand in the ring of a tripod in such a way that the level of the air-bath can be adjusted so as to control the level of the liquid in the viscosimeter itself, which is contained in the upper portion of the bath. In order to lose as little as possible of the heat supplied by a Bunsen burner, the flame is made to impinge on the arched copper plate *b*, isolated by a sheet of asbestos. Above this is placed the tripod *c* and the measuring vessel *e*, supported by *d*, and protected from direct radiation from *b* by the asbestos plate *f*.

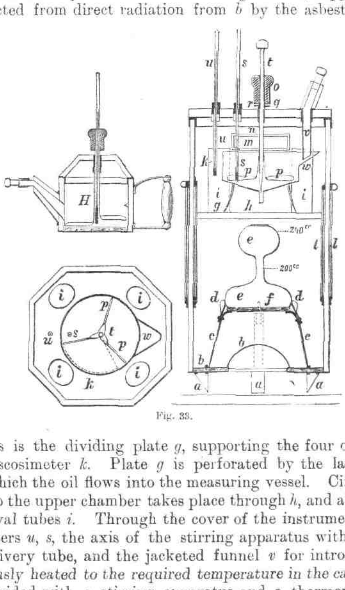


Fig. 33.

Above this is the dividing plate *g*, supporting the four oval tubes *i* and the viscosimeter *k*. Plate *g* is perforated by the large hole *h*, through which the oil flows into the measuring vessel. Circulation of hot air into the upper chamber takes place through *h*, and also through the four oval tubes *i*. Through the cover of the instrument pass the thermometers *u*, *s*, the axis of the stirring apparatus with the plug *t* for the delivery tube, and the jacketed funnel *v* for introducing the oil, previously heated to the required temperature in the can H, which is also provided with a stirring apparatus and a thermometer fixed in its hollow axis. In the cover and also in the side windows *l* and *m* are fixed; the latter permit observations to be made of the level of the oil in the viscosimeter and of the flow of the oil into the measuring vessel *e*.

[1] *Journ. Soc. Chem. Ind.* 1890, 654.

The method of using the instrument and the manipulations required for making an observation need no detailed description. That the apparatus satisfies the required condition of constant temperature is proved by the following observation of its designers. If the viscosimeter—without any charge of oil in *k*—be heated to 100° C., the temperature in all parts of the bath is equal and constant, with the exception of the lowest stratum of air in *k* itself, owing, no doubt, to the absence of any circulation. This drawback, however, disappears with the introduction of oil. At temperatures exceeding 100° C., the air above the oil vessel has a somewhat lower temperature, but the difference does not amount to more than 4° C. at 150° C.[1]

A description of *Künkler's* viscosimeter for the examination of small quantities of lubricating oils will be given in Chapter XV.

Traube[2] condemns the viscosimeters described here on the grounds that, according to theory, it is not permissible to compare directly the respective times of delivery of heavy and light oils, and still less the times of delivery of oils and water observed in one and the same apparatus. For a description of the apparatus by which *Traube* proposes to replace the viscosimeters in use, the reader must consult the original paper.

The viscosimetric examination of fatty oils does not lead to results of a discriminative nature; sperm oil, a liquid wax, alone is very characteristic in this respect (chap. xiv.).

The following tables give the viscosities of sperm oil, of some fatty oils, and of mineral oils largely used for lubricating purposes :—

Viscosities of some Oils and Fats (Crossley and Le Sueur)

Kind of Oil.	Number of Seconds in Redwood's Viscosimeter, 50 c.c. of water at 70° F. = 25·4 Seconds.	Kind of Oil.	Number of Seconds in Redwood's Viscosimeter, 50 c.c. of water at 70° F. = 25·4 Seconds.
Linseed	212	Garden cress	322
Tung oil	858-1433	Radish seed	385
	(water 28 sec.)	Arachis	307-429
Walnut	232	Olive	312
Safflower	249·1-294	Mahua	90-107
Poppy seed	254-259	Phulwara	110·4
Amoora	376	Malabar tallow	101-104
Niger seed	263-293	Kokum butter	101
Argemone	269-272	Cocoa nut oil	64

[1] A similar principle is made use of in *Marten's* viscosimeter, *Mitth. Königl. Technisch. Versuchsanst.* Berlin, 1889, Ergänzungsheft, V. 6.

[2] *Journ. Soc. Chem. Ind.* 1887, 414.

[TABLE

50 c.c. of water at 60° F. requiring 25·5 seconds.										
°F.	Rape Oil Refined.	Sperm Oil.	Neat's foot Oil.	Beef Tallow.	American Mineral Oil.			Russian Mineral Oil.		
					Sp. gr. 0·885.	Sp. gr. 0·913	Sp. gr. 0·923.	Sp. gr. 0·909.	Sp. gr. 0·915.	Sp. gr. 0·884.
50	712·5	...	...	...	145·0	425·0	1030·0	2040·0	2520·0	
60	540·0	177·0	470·0	...	105·0	295·5	680·0	1235·0	1980·0	
70	405·0	136·8	366·0	...	90·0	225·0	485·0	820·0	1320·0	
80	326·0	113·0	280·0	...	73·0	171 0	375·0	580·0	900·0	
90	260·0	96·0	219·25	...	63·5	136·0	262·0	426·0	640·0	
100	213·5	80·5	174·75	...	54·0	111·0	200·0	315·0	440·0	1015·0
110	169·0	70·5	147·4	...	50·0	89·5	153·0	226·0	335·0	739·5
120	147·0	60·5	126·0	...	47·0	78·0	126·0	174·0	245·0	531·0
130	123·5	57·0	112·0	...	44·75	63·5	101·0	135·5	185·0	398·5
140	105·5	50·75	88·4	...	41·0	58·0	82 0	116·0	145·0	317·5
150	95·5	49·0	75·5	...	37·5	52·0	70·5	95·0	115·0	250·0
160	85·0	47·5	70·0	...	...	46·0	63·5	83·5	93·5	200·0
170	76·0	46·0	62·0	...	...	...	58·0	70·5	77·5	161·0
180	69·0	44·5	56·5	...	...	...	52·5	61·5	67·5	134·5
190	64·5	43·0	53·0	...	...	...	47·0	56·5	61·0	115·5
200	58·5	42·0	50·4	54·75	...	...	42·0	48·5	54·0	99·25
210	54·0	40·75	48·5	...	...	...	40·0	...	...	85·0
220	50·0	39·0	47·0	...	...	...	38·0	...	...	77·0
230	47·25	36·75	45·8	...	...	...	...	...	...	70·5
240	45·5	35·75	44·6	...	...	...	...	...	...	64·5
250	43·25	34·75	44·0	40	...	...	...	...	...	59·25
260	...	33·75	43·5	...	...	...	...	...	...	54·0
270	...	32·75	43·0	...	...	...	...	...	...	48·5
280	...	31·85	41·5	...	...	...	...	...	...	46·5
290	...	30·75	41·0	...	...	...	...	...	...	44·25
300	...	30·0	38·0	...	...	...	...	...	...	42·4
310	...	...	35·0							
320	...	...	33·8							

Kind of Oil.	Specific Gravity at 15·5° C.	Number of Seconds required at		
		15·5° C.	50° C.	100° C
Sperm oil	0·881	80	47	38
Seal oil (pale)	0·924	131 (?)	56 (?)	43 (?)
Northern whale oil	0·931	186	65	46
Menhaden oil	0·932	172	40	...
Sesamé oil	0·921	168	65	50
Arachis oil	0·922	180	64	...
Cotton seed oil (refined)	0·925	180	62	40
Niger seed oil	0·927	176	59	43
Olive oil	0·916	187	62	43
Rape oil	0·915	261	80	45
Castor oil	0·965	2420	330	60

	Specific Gravity at 60° F.	Viscosity (Redwood's Viscosimeter).			Flash Point. Close Test.	Cold Test.		
		70° F.	120° F.	180° F.	°F.	°F.		
		Standard for Viscosity. Sperm Oil at 70° C. = 100.						
Refined Mineral Oils—[1]								
Scotch	0·890-0·895	100-130	40-50	..	320-350	32		
	0·885-0·890	75-100	35-40	..	300-325	32		
	0·875-0·880	50-60	25-30	..	300-325	32		
American	0·915-0·920	400-425	90-100	35-40	375-425	32		
	0·905-0·910	200 225	55-65	..	350-400	32		
	0·885-0·890	75-100	35-40	..	325-350	32		
	0·875-0·880	65-75	30-35	..	325-350	32		
Russian	0·910-0·915	1200-1500	200-250	50-70	400-425	25		
	0·905-0·912	700-800	125-150	45-50	350-375	25		
	0·895-0·900	220-250	60-65	..	325-350	15		
	0·895-0·900	125-175	..	..	300-325	10		
		Standard for Viscosity. Tallow at 180° C = 100.						
Natural (dark) Mineral Oils—								
American summer, dark	0·890-0·895	..	250-300	70-75	400-425	40-50		
,, medium	0·880-0·885	550-700	110-125	40-50	350-400	25-30		
,, winter	0·880-0·885	350-400	90-100	35-40	325-375	25-30		
Russian residuum	0·910-0·915	750-1000	150-200	45-60	250-300	25-30		
Natural and Filtered Mineral Oils—								
American heavy dark	0·900-0·905	..	1750-2000	350-400	500-550	40-45		
,, extra dark	0·900-0·905	..	2000-2500	400-450	525-575	35-40		
,, medium dark	0·895-0·900	..	1200-1400	300-350	500-525	40-45		
,, heavy filtered	0·890-0·895	..	1400-1500	300-350	500-550	60-70		
,, medium filtered	0·890-0·895	..	1000-1200	250-300	500-525	65-70		
,, light filtered	0·885-0·890	..	885-1000	200-250	450-500	75-80		
,, fluid filtered	0·885-0·890	..	1200-1400	300-350	500 550	40-45		
,, ...	0·885-0·890	..	900-1000	225-275	450-500	45-50		
							No. of Samples	Flash Points, °F.
Southern sperm oil	0·8807	100·1	45·4	..	457·5*	41·7	34	420-485
Arctic sperm oil	0·8804	105·8	47·2	..	446·2*	39·2	59	390-485
White whale oil	0·9207	187·7	71·3	..	476·0*	27·2	35	430-530
Neat's foot oil	0·9178	247	82·4	..	470·3*	34·4	17	410-540
Lard oil	0·9172	223·2	79·4	..	493·9*	39·6	18	425-545
Olive oil	0·9167	213·2	75·0	..	437·5*	27	24	410-465
Rape oil, East India, refined	0·916	250·4	88·1	..	478·6*	26·4	89	410-510
,, Black Sea, refined	0·9209	226·9	78·8	..	465·4*	27	25	430-490
Cotton seed oil, refined	0·9235	190·4	69·8	..	523 *	30	22	500-540
Castor oil	0·963	2500	390	..	487 *	0		

[1] Carpenter-Leask, pp. 263-291.

* Mean Values.

Kind of Oil or Fat.	Specific Gravity at 17·5° C.	Viscosity (Engler's Viscosimeter).			
		20° C.	50° C.	100° C.	150° C.
Rape oil, crude	0·920	9·03	4·0	1·78	1·34
Rape oil, refined	0·911	11·88	4·9	2·05	1·40
Olive oil	0·914	10·3	3·78	1·80	
Castor oil	0·963	...	16·46	3·01	
Linseed oil	0·930	6·36	3·2	1·76	
Tallow	0·951	...	5·19	2·50	1·73
Neat's foot oil	0·916	11·63	4·44	1·92	

Oils.	Specific Gravity at 17·5° C.	Flash Point. °C.	Viscosity (Engler's Viscosimeter).	
			At 50° C.	At 100° C.
Russian cylinder oils	0·911-0·923	183-238	10·2-16·2	2·0-2·8
,, machine oils	0·893-0·920	138-197	5·8-6·3	1·5-1·8
,, spindle oils	0·893-0·895	163-167	3·1-3·4	1·4-1·5
American cylinder oils	0·886-0·899	280-283	...	4·1-4·8
,, machine oils	0·884-0·920	187-260	4·2	1·6
,, spindle oils	0·908-0·911	187-200	3·1-3·3	1·4-1·6
Rape oil, crude	0·920	265	4·0	1·7
,, ,, refined	0·911	305	4·9	2·0
Olive oil	0·914	305	3·7	1·8
Castor oil	0·963	275	16·4	3·0
Linseed oil	0·930	285	3·2	1·7
Tallow	0·951	265	5·2	2·5

Crossley and *Le Sueur*[1] have drawn attention to a correlation between the viscosity and the iodine numbers, as shown in the following table:—

Kind of Oil.	Iodine Value.	Viscosity (Redwood's Viscosimeter). Number of Seconds at 70° F.
Arachis	92·43	429·3
	98·42	347·0
	98·47	350·1
	100·82	306·9
Argemone	119·91	272·0
	122·53	268·9
Rape	94·10	464·6
	96·66	413·8
	96·75	402·0
	96·25	393·2
	101·82	379·3
	101·84	371·8

This correlation is, however, not borne out by the numbers recorded in the preceding tables.

5. Rotatory Power of the Plane of Polarisation

Vegetable fatty oils, with the exception of castor oil, rotate the plane of polarised light very slightly only, as is shown by the following table, which reproduces *Bishop's*[2] observations taken in a *Laurent's* saccharimeter with a 20 cm. tube.

[1] *Journ. Soc. Chem. Ind.* 1898, 990. [2] *Ibid.* 1887, 750.

Kind of Oil.	Rotation in Saccharimeter. Degrees.
Almond oil, sweet	−0·7
Arachis oil	−0·4
Colza (French) oil	−2·1
,, (Japanese)	−1·6
Linseed oil	−0·3
Walnut oil	−0·3
Poppy seed oil	0·0
Olive oil	+0·6
Sesamé oil, cold expressed	+3·1
,, ,, warm expressed	+7·2
,, ,, 1878	+4·6
,, ,, 1882	+3·9
,, ,, 1882	+9·0
,, ,, Indian	+7·7

Peter,[1] who has also examined a number of oils by means of *Laurent's* saccharimeter, found that almond, rape, hemp seed, linseed, and poppy seed oils are lævo-rotatory, while some samples of arachis oil were dextro-rotatory, others again lævo-rotatory. But with regard to almond, rape, linseed, arachis, and poppy seed oils *Thoerner*,[2] who examined these oils in a 20 cm. tube in *Wild's* Polaristrobometer, leaves it open to doubt whether definite rotation occurs. The same chemist gives for castor and sesamé oils the numbers + 6·4° and + 1·0° *respectively*.

Fatty acids, according to *Peter*, have the same optical activity as the oils from which they have been derived. This has been confirmed by *Thoerner* for castor oil and sesamé oil fatty acids, and by *Walden* for castor oil.

It is very likely that, with the exception of castor oil, the rotatory power of which is explained by the asymmetric carbon-atom of the ricinoleic acid, the optical activity is not due to the glycerides themselves, but to small proportions of optically active substances, such as phytosterol. *In the case of sesamé oil, at all events, the optical* activity must be due to phytosterol and sesamin. As such substances[3] are isolated together with the fatty acids, the optical activity of the fatty acids is readily explained.

From the foregoing notes, it will be gathered that very little information of a discriminative nature can be obtained from the polarimetric examination of oils and fats. This method of examination will, therefore, only be resorted to in exceptional cases, as in the examination of linseed oils. In that case strong deviation of the polarised light to the right may reveal the presence of rosin oil.

6. Microscopic Appearance

Although the microscope has been frequently recommended for the examination of fats and the detection of adulterants, micro-

[1] *Bull. Soc. Chim.* 1887, 483. [2] *Journ. Soc. Chem. Ind.* 1895, 43.
[3] Cp. also Stillingia Oil, chap. xiv.

scopical examination has hitherto been of limited use only. Until recently it had been chiefly employed in the detection of beef fat in lard. On dissolving beef fat in ether and allowing it to crystallise, crystals were obtained differing in shape from crystals obtained in the same manner from lard. It was generally assumed that beef-fat crystals consisted preponderantly of stearin, which would crystallise first from a mixture of glycerides, whereas lard being much poorer in contents of stearin, yielded crystals differing in shape.

The importance of this difference has been much weakened, since it has been shown that the lard crystals, on repeated crystallisation, approximate to the form of beef-fat crystals, and furthermore since mixed glycerides have been discovered in fats.

Microscopic examination becomes of much greater use if it is a question of differentiating between cholesterol and phytosterol (*Bömer*) (cp. chap. ix.).

The application of the polarisation microscope to the examination of oils and fats is, up till now, more restricted still in its practical application.

7. Spectroscopical Examination

With the exception of palm oil, the more important oils and fats are whitish or yellowish; it is therefore impossible to detect any characteristic differences with the naked eye. On examining, however, the fats spectroscopically, characteristic absorption spectra are obtained. Although they are not due to the fatty substance itself, but to the presence of minute quantities of colouring matters, they serve in some instances to distinguish different oils. Thus an admixture of vegetable oils with those of animal origin may be detected by the characteristic absorption bands which chlorophyll produces. Olive oil and linseed oil give three absorption bands—a very dark one in red, a faint one in orange, and a distinct one in green. Sesamé oil produces a weak band in red, whilst castor oil gives no bands at all.[1]

Chautard has subdivided the oils into two classes, active and inactive, according as they absorb certain prismatic colours, or allow them to pass through unabsorbed.

Doumer groups the oils, according to their spectroscopical behaviour, into four classes :—

1. Oils showing the spectrum of chlorophyll: olive oil, hemp seed oil, and nut oil.
2. Oils without any light-absorbing power: castor oil and almond oils.
3. Oils absorbing the "chemical rays" of the spectrum, the red, orange, yellow, and part of the green remaining unabsorbed. On examining such oils the spectrum from red to green appears, therefore, quite normal, whilst the other parts are invisible. To this class belong rape oil, linseed oil, and mustard seed oil.

[1] Vogel, *Practische Spectralanalyse*, 1877, 279.

4. Oils showing absorption bands in the different parts of the spectrum: sesamé oil, arachis oil, poppy seed oil, and cotton seed oil.[1]

Zune, who has resumed the study of the spectroscopic behaviour of oils, adopts *Chautard's* classification.[2]

8. Consistence

It has been pointed out already that any attempt to base a classification of oils, fats, and waxes on the consistence must lead to failure.

Methods employing consistence as a means of examination have very limited application, and can at best only be used to discriminate various specimens of one and the same oil. But even in *those cases, the determination of the solidifying and* melting points of the oils themselves, or of their fatty acids, will lead to more decisive results.

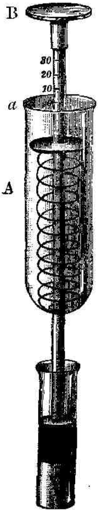


Fig. 34.

The first attempts to employ the determination of consistence for analytical purposes were made by *Serra Carpi* and by *Legler*; in both cases the method was proposed in the first instance for the examination of olive oil.

Serra Carpi[3] cools the olive oil down to − 20° C. for three hours, and places on the solidified fat, by means of a suitable arrangement, a cylindrical iron rod 2 mm. in diameter and 1 cm. long, and conical at the bottom. Weights are then put on the rod until it sinks completely into the fat. Thus, for pure olive oil 1700 grms. were required; a sophisticated oil required 1000 grms. only, whereas for cotton seed oil 25 grms. were found to be sufficient.

Whilst *Serra Carpi* examines the oil itself, *Legler* treats it previously with nitrous acid so as to produce the harder elaïdin (see Elaïdin Test). He recommends the apparatus shown in Fig. 34. This consists of a strong glass tube A, in which a strong glass rod is allowed to slide. The rod is widened at *a* into a disc holding down the spring, which easily responds to a weight of 20-50 grms. placed on the top B. The point to which the glass rod slides down by its own weight is marked by 0 on the rod; from there upwards, marks indicating millimeters are scratched into the rod. Substantially the same principle and the same apparatus have been recommended by *Brullé*[4] (for the examination of butter) and by *Sohn*.[5] The latter proposes three forms of apparatus, and lays down the following rules, to which strict adherence is necessary:—

[1] Cp. Kenrick, *Analyst*, 1895, 136.
[2] *Analyse des Beurres*, ii. 48.
[3] *Zeit. f. Analyt. Chem.* 23, 566.
[4] *Journ. Soc. Chem. Ind.* 1893, 717.
[5] *Analyst*, 1893, 218.

(1) The rod must descend in an absolutely perpendicular direction.
(2) It must slide in its bearing with the least possible friction.
(3) Conditions of temperature must be constant.
(4) Vessels of one diameter must be used for the material under examination.
(5) The rod must enter the centre of the vessel, or at a fixed distance from the circumference.
(6) The same depth of material must always be used.
(7) The material must be allowed to rest a certain fixed time before testing.

9. Solubility

It has been pointed out already (p. 18) that oils and fats dissolve readily in ether, carbon bisulphide, chloroform, carbon tetrachloride, benzene, petroleum, and petroleum ether.

The differences as regards solubility are not so pronounced that the various oils and fats can be thereby differentiated.

Castor oil, however, differs from all other natural oils and fats in two respects: firstly, by its solubility in alcohol, and secondly, by its comparative insolubility in petroleum ether and paraffin oil. All other oils and fats are nearly insoluble, or very sparingly soluble in alcohol at the ordinary temperature.

The solubility of most oils and fats in absolute alcohol at about 15° C. does not exceed 2 per cent. The solubility in 96 per cent alcohol, or in more dilute alcohol, is smaller still.

Oils and fats containing glycerides of the lower fatty acids, such as porpoise oil, cocoa nut oil, palm nut oil, butter fat, are somewhat more soluble in alcohol than those oils and fats which consist chiefly of the glycerides of oleic, palmitic, and stearic acids. Also oils consisting to a large extent of the glycerides of linolic and linolenic acids, as *e.g.* linseed oil, exhibit a slightly increased solubility in alcohol.

Since the solubilities in alcohol do not afford any discriminating value, the isolated determinations made by *Girard* and others need not be enumerated here. Besides, the numbers given by various observers are hopelessly discordant. This may be partly due to the presence of free fatty acids, whereby the solubility in alcohol is considerably increased. Alcoholic solutions of free fatty acids dissolve neutral oils and fats readily; as a rule, oils containing more than 50 per cent of free fatty acids are completely soluble in alcohol. Thus, until recently olive kernel oil was described as soluble in alcohol, but it has been shown that the alleged solubility was solely due to the large proportion of free fatty acids in the samples examined originally.

At higher temperatures the solubility in alcohol increases, and under suitable conditions of pressure and concentration of alcohol, and above a definite temperature, glycerides form a homogeneous mixture with it. The temperature at which the mixture will just separate into its component parts is termed by *Crismer* the critical

temperature of dissolution. It is analagous to the critical temperature of gases.

Crismer[1] proposed the determination of the critical temperatures of dissolution as a means of differentiating oils and fats, and especially of distinguishing butter fat from those fats that are likely to be used in adulterating it.

Crismer places a few drops of the oil or melted fat in a glass tube 9 cm. long and 5-6 mm. wide, and adds about twice the volume of 90 per cent alcohol. The tube is then sealed and fixed by means of a platinum thread to the bulb of a thermometer, and heated in a bath of sulphuric acid or glycerin, until the meniscus separating the two layers has become flattened into a plane. After heating a little longer, so as to allow the temperature to rise, say, another 10° C., the thermometer is withdrawn from the bath and rapidly turned up and down several times. It is then placed in the bath and the tube observed carefully, whilst the thermometer is being gently shaken. The temperature at which a marked turbidity appears is recorded as the critical temperature of dissolution.

If the critical temperature does not exceed the boiling point of alcohol, 78° C., an open tube may be used in place of a sealed one. Thus in the case of butter fat 0·5 c.c. of the filtered fat is placed in a tube 7 to 8 cm. long and about 1 cm. in diameter, with twice its volume of absolute alcohol. The tube is provided with a cork, fitted with a thermometer, the bulb of which is immersed wholly in the liquid on inserting the cork into the tube. The tube is gently heated in a larger tube, serving as an air-, or water-bath, until by agitating the contents vertically a homogeneous liquid is obtained. The mixture is then allowed to cool, and the critical temperature is determined as described above.

This method has been used hitherto chiefly in the examination of butter (chap. xiv.).

The critical temperature of dissolution of a mixture is, according to the same author, approximately the arithmetical mean of those of its constituents; it may be calculated from the following formula :—

$$T_m = \frac{nT_a + (100 - n)T_b}{100},$$

where

T_m = the critical temperature of the mixture.
T_a = the critical temperature of the constituent a.
T_b = the critical temperature of the constituent b.
n = the volume of constituent a in 100 volumes.
$100 - n$ = the volume of constituent b in 100 volumes.

From the experiments made hitherto, the further deduction has been derived that substances of the same nature have practically the same critical temperature of dissolution.

The observations recorded hitherto are collated in the following table :—

[1] *Bulletin de l'Assoc. Belge des Chimistes*, 1895, ix. 71, 143 ; 1896, ix. 359 ; x. 312.

Critical Temperatures obtained with Alcohol, Specific Gravity 0·8195, *at* 15·5° *C.*

Substance.	No. of Samples.	°C.	Observer.
Japanese fish oil	...	108	Crismer and Motteu[1]
Cotton seed oil	...	115-116	Herlant[2]
Colza oil	...	132-135	Crismer and Motteu
Sesamé oil	...	120·5	Herlant
Arachis oil	1	115-116	,,
Arachis oil	2	123	,,
Olive oil	...	123	,,
"Animal" oil	...	120	Crismer and Motteu
Sheep's foot oil	...	102	,,
Neat's foot oil	...	95	,,
Lard oil	...	104	,,
Apricot kernel oil	1	47·7	Dieterich
Cocoa nut oil	...	71-75	Crismer
Cacao butter	...	126	,,
Butter fat	14	98-102	,,
Butter fat	4	98-103	Herlant
Margarine	...	122-126	Crismer
Carnaüba wax	...	154	,,
Beeswax	from various sources	129-133	,,
Ozokerit	...	175	,,
Paraffin wax	according to constitution and melting points	140-160	,,
Oil of turpentine	...	14	,,

By using more dilute alcohol higher values are obtained for the critical temperatures, as will be seen from the following table, due to *Asbóth* :[3]—

Critical Temperatures with Alcohol of 90 *per cent by volume, Specific Gravity* 0·8332

	No. of Samples.	Becomes perfectly clear at °C.	Commences to become cloudy at °C.	Commences to form 2 layers at °C.	Critical Temperature. °C.
Butter fat	7	119-134	117·5-131	113·5-120	111·5-115
Butter fat	1	124	121	116	115
Margarine	2	140-151	138-148	135-144·5	133·5-142

[1] *Journ. Soc. Chem. Ind.* 1896, 300.
[2] *Ibid.* 1896, 562.
[3] *Chem. Zeit.* 1896, 685.

If absolute alcohol be employed, an open tube may be used. The results obtained for butter fat will be given in Chapter XIV. under "Butter Fat."

Valenta[1] classifies the fatty oils and solid fats into three groups according to their solubility in **acetic acid.** The test is carried out by thoroughly mixing equal volumes of oil or fat and glacial acetic acid of specific gravity 1·0562 in a test-tube, and warming the mixture in case no solution has taken place.

1st Class.—Completely soluble at the ordinary temperature (14° to 20° C.): Castor oil.

2nd Class.—Completely soluble, or nearly so at temperatures ranging from 23° C. up to the boiling point of glacial acetic acid: Pumpkin seed oil, cotton seed oil, sesamé oil, apricot kernel oil, almond oil, arachis oil, olive oil, cod liver oil, laurel oil, mowrah seed oil, palm oil, nutmeg butter, cacao butter, palm nut oil, cocoa nut oil, bone fat, beef tallow, butter fat, beef stearine.

3rd Class.—Not completely dissolved—even at the boiling point of glacial acetic acid—the oils obtained from seeds of the *Cruciferæ*: Rape seed oil, mustard seed oil, hedge mustard oil, etc.

The oils belonging to the second class may be further differentiated by gradually warming the sample with an equal volume of glacial acetic acid in a test-tube with frequent shaking until complete solution is effected. A thermometer is then introduced into the liquid, and the temperature noted at which turbidity appears. According to *Valenta*, the fats of the second class may be subdivided into two groups: the one embracing the following fats—palm oil, laurel oil, nutmeg butter, cocoa nut oil, palm nut oil, and mowrah seed oil; the remaining oils of that class form the second group. The temperatures found by *Valenta* are given in the following table.

Allen's[2] observations, however, as will be seen from the table, are not in agreement with those recorded by *Valenta*.

[1] *Journ. Soc. Chem. Ind.* 1884, 643. [2] *Ibid.* 1886, 69; 282.

[TABLE

Solubility of Fatty Oils and Solid Fats in Acetic Acid

Kind of Oil or Fat.	Temperature of Turbidity for equal Volumes of Oil or Fat and Glacial Acetic Acid, spec. grav. 1·0562.	
	Valenta.	Allen.
	°C.	°C.
Linseed oil	...	57-74
Niger seed oil	...	49
Pumpkin seed oil	108	
Cotton seed oil	110	90
Sesamé oil	107	87
Apricot kernel oil	114	
Almond oil, sweet	110	
Arachis oil	112	87
Yellow olive oil	111	
Green olive oil (of second expression)	85	
Menhaden oil	...	64
Cod liver oil	101	79
Shark liver oil	...	105
Seal oil	...	72
Whale oil	...	38, 86
Porpoise oil	...	40
Neat's foot oil	...	102
Laurel oil	26-27	40
Mowrah oil	64·5	
Palm oil	23	83
Nutmeg butter	27	39
Cacao butter	105	Insoluble
Palm nut oil	48	32
Cocoa nut oil	40	7·5
Lard	...	96·5
Bone fat (American)	90-95	
Beef tallow	95	
Oleomargarine	...	96·5
Butter fat	...	61·5
Tallow stearine (M. P. 55·8°)	114	
Sperm oil	...	98-103
Arctic sperm oil	...	102

The following table, comprising oils belonging to *Valenta's* third class, more clearly demonstrates the same point :—

Kind of Oil.	Specific Gravity at 15·5° C. (water at 15·5=1).	Observer.		
		Valenta.	Allen.	Hurst.
				°C.
Rape	0·9145	Insoluble	Insoluble	88
Rape	0·9168	,,	,,	86
Rape	0·9132	,,	,,	85
Rape	...	,,	,,	73
Colza	0·9162	,,	,,	99
Colza	0·9131	,,	,,	97
Colza	...	,,	,,	94
Colza	...	,,	,,	94
Colza	0·9132	,,	,,	82

Thomson and *Ballantyne*,[1] experimenting with acetic acids of different strengths, arrived at the following numbers :—

Kind of Oil	Free Acid calculated as Oleic Acid.	Temperature of Turbidity with Glacial Acetic Acid of		
		Sp. Gr. 1·0542.	Sp. Gr. 1·0552.	Sp. Gr. 1·0562.
	Per cent.	°C.	°C.	°C.
Olive oil (Gioja) . . .	9·42	65	80	91
Same oil, freed from free acid	none	87	...	...
Olive oil (Syrian) . .	23·88	42	...	...
Olive oil	5·19	78	96	...
	3·86	85	100	111
Arachis oil (commercial) .	6·20	76	92	112
Arachis oil (French, refined)	0·62	96	114	Not completely dissolved
Rape oil	2·43	110	Not completely dissolved	...
	4·54	105	...	...
Linseed oil	0·76	61	78	[illegible]
Linseed oil (Baltic) . .	3·74	42	59	71
Linseed oil (East India) .	0·79	57	...	...
Linseed oil (River Plate) .	1·21	56	...	...

The indications of the last table prove that the amount of free fatty acid in fats considerably influences the indications of *Valenta's* test.

Notwithstanding these serious discrepancies, *Valenta's* test may, in conjunction with other tests, afford some valuable hints in the examination of an oil.

The following modification of *Valenta's* test has been proposed by *Jean* :[2]—Place 3 c.c. of the fat in a graduated test-tube of 1 cm. diameter, and immerse the tube in water of 50° C. Remove, by means of a finely drawn-out pipette, so much oil that exactly 3 c.c. remain (at the temperature of 50° C.). Next introduce, by means of a graduated pipette, 3 c.c. of acetic acid, specific gravity 1·0565 at 15° C. (prepared from glacial acetic acid by adding the requisite amount of water), the acid being measured off at 22° C., warm the contents of the tube in the water for a few minutes, then cork well, and agitate thoroughly. Allow the mixture to settle out at 50° C. until two distinct layers are noticeable, and read off the volume of the undissolved acetic acid. The volume of the acid dissolved in the fat is then easily calculated. *Jean* has found the following proportions for the oils and fats given in the table :—

[1] *Journ. Soc. Chem. Ind.* 1891, 233.
[2] *Corps gras industriels*, 1892 [19], 4.

Kind of Oil or Fat.	Acetic Acid (sp. gr. 1·0565 at 15° C.) dissolved. Per cent.
Arachis oil (Boulam)	41·65
Arachis oil (Gambia)	43·66
Colza oil	30·00
Ravison oil	33·30
Almond oil, sweet	33·00
Olive oil	*35·00*
Walnut oil	36·60
Cameline oil	36·60
Castor oil	100·00
Maize oil	100·70
Beech nut oil	53·3
Poppy seed oil (India)	63·3
Poppy seed oil (French)	43·3
Neat's foot oil	43·3
Sheep's foot oil	36·66
Horse fat	30·08
Lard	26·66
Veal tallow	26·66
Butter, 9 samples of different origin	63·33 [1]
Cotton seed stearine	*40·00*
"Butterine"	31·60
Margarine	26·66
Palm oil	100·00
Cocoa nut oil	100·00

For further information the reader must be referred to the article on "Butter Fat," chap. xiv.

The behaviour of some oils with carbolic acid has been studied by *Salzer*.[2] The test is carried out by adding the oil drop by drop to 10 c.c. of a phenol solution, prepared from 373 grms. of crystallised phenol and 56·7 grms. of water,[3] *contained in a graduated cylinder with constant shaking, until the turbidity persists. In liquefied* phenol of a higher strength than 91 per cent, most oils seem to be equally soluble, important differences only appearing on employing weaker solutions. In the following table *Salzer's* results are reproduced:—

[1] Besides these nine samples, all of which gave 63·33 per cent, two abnormal butters were examined, giving 58·7 and 73·0 respectively.

[2] *Arch. d. Pharmac.* 227, 433.

[3] This solution was first suggested by Crook (*Zeit. analyt. Chemie* 19, 369).

[TABLE

Kind of Oil.	Dissolved by 10 c.c. of Phenol of		
	91 per cent.	87 per cent.	83 per cent.
	c.c.	c.c.	c.c.
Almond oil	...	Min. 2·5 Max. 3·5	
Olive oil	...	Min. 2·0 Max. 3·0	
Rape oil	4	...	
Linseed oil	...	...	3
Poppy seed oil	...	6·8	Min. 2
Croton oil	16	8·5	4·0
Arachis oil	11·5	4·3	0·8
Cotton seed oil	10·5	5·5	1·0
Sesamé oil	10	3·8	0·8
1 part of olive oil + 1 pt. of poppy seed oil	...	4·8	
3 parts of olive oil + 1 pt. of poppy seed oil	...	3·4	
3 parts of olive oil + 1 pt. of arachis oil	...	3·0	
1 part of olive oil + 1 pt. of arachis oil	...	3·8	
9 parts of olive oil + 1 part of rape oil	...	2·1	
Croton oil	...	Distinct turbidity with 2·3	

Salzer claims to be able to detect adulterants in almond oil, cod liver oil, etc. The figures recorded in the table are, however, not such as inspire confidence in this method; moreover, free fatty acids increase the solubility. *Salzer's* method can, therefore, at best only serve as a preliminary test.

Bach[1] proposed to examine the mixed fatty acids with regard to their solubilities in *David's* alcohol-acetic-acid-mixture (cp. p. 354). Since, however, the indications furnished by this test do not afford any definite information, his statements need not be detailed here.

The following table gives the solubilities of some mixed fatty acids in absolute alcohol:—

Solubility of Mixed Fatty Acids in Absolute Alcohol

Mixed Fatty Acids from	100 grms. of Absolute Alcohol dissolve	
	at 0° C.	at 10° C.
	Grms.	Grms.
Mutton tallow	2·48	5·02
Beef tallow	2·51	6·05
Veal tallow	5·00	13·78
Lard	5·63	11·23
Butter fat	10·61	24·81
Margarine	2·37	4·94

[1] *Pharm. Centralhalle*, 1883, 159.

The solubility of some fats in benzene has been determined by *Dubois* and *Padé*. Their numbers are given in the following table:—

Solubility of Solid Fats in Benzene

Kind of Fat.	100 grms. of Benzene dissolve at 12° C.
	Grms.
Mutton tallow	14·70
Beef tallow	15·89
Veal tallow	26·08
Lard	27·30
Butter fat	69·61
Margarine	12·83

10. Electrical Conductivity

The determination of the electrical conductivity has been proposed by *Palmieri*[1] as a means of detecting the sophistication of olive oil. For this purpose he constructed a special apparatus termed "diagometer."

Later on *A. Bartoli*[2] made an extensive examination of the electrical conductivity of oils and fats; the following are the main results:—The conductivity of an oil increases with the rise of temperature, its amount, however, varying with the nature of the oil. The drying oils, when exposed to the air, acquire a greater conductivity than the non-drying oils. An increase, though to a smaller extent, is also observed in the case of the non-drying oils, when they are rancid. A table, arranged according to the magnitude of the electrical conductivity, begins with olive oil and ends with linseed oil.

The solid fats, with the exception of lard, exhibit increase of conductivity at temperatures from 170° to 220° C. Nutmeg butter is characterised by a sudden increase at the temperature of its melting point. A similar table of conductivities for the solid fats opens with chicken fat and closes with nutmeg butter.

The measurement of the electrical conductivity of the potash soaps obtained by saponifying an oil or fat under examination was proposed by *L. Herlant*.[3] It is, of course, essential to employ in each case the same amount of fat and alkali, and to dilute the solutions to exactly the same strength, and also to make all observations at one and the same temperature. For the examination 10 grms. of an oil or fat are mixed in a flask with 45 c.c. of pure normal alcoholic potash and saponified by heating for thirty minutes on the waterbath, the flask being attached to a reflux condenser. The alcoholic soap solution is then made up with distilled water to 250 c.c. and electrolysed.

[1] *Rend. della Acc. di Napoli*, 1881. [2] *Il nuovo Cimento*, 1890, tomo 28. 25.
[3] *Journ. Soc. Chem. Ind.* 1896, 562.

The resistance which a cube with a side of 1 cm., filled with the solution, offers is the *specific resistance* r of this solution, and its inverse ratio $\frac{1}{r}$ expresses its *specific conductivity*. For practical purposes comparison is made with the specific conductivity of a $\frac{1}{500}$ norm. solution of potassium chloride, for which $\frac{1}{r} = 0·002244$ at 18° C. If K be a coefficient depending on the trough, then we have for the potassium chloride solution $\frac{1}{r}K = 0·002244$, and for the specific conductivity of any other solution in this trough $l = \frac{1}{r_1} \times K$.

The numbers obtained by *Herlant* are given in the following table. A few values for butter fat and margarine are added here, as *Herlant* believes that this method may be useful in the examination of butter. The third and fourth columns are added in order to show that the conductivity stands in direct relation to the refractive index and critical temperature :—

Oil or Fat.	Specific Conductivity at 18° C.	Refractive Index. Degrees in Zeiss's Butyro-refractrometer at 35° C.	Critical Temperature of Dissolution. °C.
Cotton seed	0·008629	63	115-116
Arachis I.	0·008700	58·25	115-116
,, II.	0·008741	60·25	123
Sesamé	0·008779	63	120·5
Olive	0·009927	57·25	123
Butter fat 1	0·006457	98-103	44·5
,, 2	0·006500		45
,, 3	0·006507		45
,, 4	0·007010		48
Margarine 1	0·008221	122-123	52·5
,, 2	0·008459		56·5
,, 3	0·008472		54
,, 4	0·008489		58

11. Calorimetric Examination

The calorimetric examination of oils and fats will not find application in practical work, as the meagre information furnished by this test is altogether out of proportion to the labour involved in making the determination. As will be seen from the following tables, this method is incapable of yielding such definite information as is readily obtained by a number of methods carried out in a much shorter time and without necessitating the use of complicated apparatus.

[TABLE

Heats of Combustion of Fatty Acids

	Calories per Gram.	Observer.
Acetic acid	206·7	Stohmann [1]
Butyric acid (normal) . .	520·4	,,
Valeric acid (normal) . .	677·2	,,
Caproic acid . . .	830·2	,,
Caprylic acid . . .	1138·7	Louguinin [2]
Capric acid	1458·3	Stohmann [1]
Lauric acid	1771·8	,,
,, ,, ...	1759·7	Louguinin
Myristic acid . . .	2085·9	,,
,, ,, . . .	2061·8	Louguinin [2]
Palmitic acid . . .	2398·4	Stohmann [1]
,, ,, . . .	2371·8	Louguinin [2]
Stearic acid . . .	2711·8	Stohmann [1]
Arachidic acid . . .	3025·8	,,
Behenic acid . . .	3338·3	,,
Erucic acid	3297·2	,,
Brassidic acid . . .	3290·1	,,
Behenolic acid . . .	3255·1	,,
Dihydroxybehenic acid .	3235·5	,,

Heats of Combustion of Glycerides

	Per 1 Molecule Constant Volume.	Observer.
Trilaurin	5707·0	Stohmann
,, ...	5707·4	Louguinin
Trimyristin	6650·5	Stohmann, etc.
,, ...	6607·9	Louguinin
Dierucin	6979·5	Stohmann
Trierucin	10265·5	Stohmann, etc.
Dibrassidin	6953·7	,,
Tribrassidin	10236·0	,,

[1] Stohmann and collaborators, Kleber, Langbein, and Offenhauer, *Journ. prakt. Chemie*, 1885 (31), 297 ; 1890 (42), 367.
[2] *Compt. rend.* 102, 1240 (1886).

[Table

Heats of Combustion of Natural Oils and Fats

	Calories per Gram.		
	Constant Volume.	Constant Pressure.	Observer.
Linseed oil (1900)	9364	9379	Sherman and Snell[1]
,, ,, (1898)	9379	9394	,,
,, ,, (several years old)	9215	9230	,,
Boiled linseed oil	8810	8824	,,
Poppy seed oil	9382	9397	,,
Maize oil (1900)	9413	9428	,,
,, ,, (1898)	9436	9411	,,
,, ,, (crude)	9419	9434	,,
Cotton seed oil I.	9396	9411	,,
,, ,, II.	9401	9416	,,
,, ,, III.	9390	9405	,,
,, ,, IV. (crude)	9397	9412	,,
,, ,, V.	9336	9351	,,
,, ,, VI. (old)	9323	9328	,,
,, ,, VII. (very old)	9168	9183	,,
Sesame oil	9395	9410	,,
Rape oil I.	9489	9504	,,
,, ,, II.	9462	9477	,,
,, ,, III.	9412	9427	,,
Castor oil I.	8863	8877	,,
,, ,, II.	8835	8849	,,
Almond oil I.	9454	9469	,,
,, ,, II.	9311	9326	,,
Arachis oil	9412	9427	,,
Olive oil I.	9457	9472	,,
,, ,, II.	9451	9466	,,
Cod liver oil (fresh)	9437	9452	,,
,, ,, (old)	9277	9292	,,
Shark liver oil (refined)	9360.	9375	,,
,, ,, (crude)	9371	9386	,,
Whale oil	9473	9488	,,
Goose fat	9503	...	Stohmann
Lard	9469	...	,,
,, (1900)	9451	9466	Sherman and Snell
,, (1899)	9447	9462	,,
,, (four to five years old)	9394	9409	,,
,, (three years old)	9372	9387	,,
Beef fat	9485	...	Stohmann
Mutton fat	9492	...	,,
Butter fat	9503	...	,,
Spermaceti	9946	9964	Sherman and Snell

[1] *Journ. Amer. Chem. Soc.* 1901, 164.

CHAPTER VI

CHEMICAL METHODS OF EXAMINING OILS, FATS, AND WAXES

SINCE the natural oils and fats represent a mixture of the glycerides of the various fatty acids enumerated in Chapter III. in varying quantities, complete fat analysis should embrace the isolation of each individual fatty acid. The attempt to detect and identify all the individual fatty acids in a similar fashion as the individual elements are detected in an inorganic substance must, in the present state of our knowledge, be abandoned as a well-nigh hopeless task. But although we are not yet able to make an examination of the oils, fats, and waxes with strictly scientific accuracy, there have been evolved a number of methods answering very satisfactorily all the requirements of technical analysis.

These methods consist in ascertaining certain numbers which depend on the nature of the various fatty acids, and since they simultaneously furnish a measure of the quantity of these acids without, however, determining their absolute quantity, these methods have been appropriately termed by *Hübl* "quantitative reactions."

I subdivide these numbers into two classes—A. *Constants*, and B. *Variables*.

Under constants I shall comprise those numbers which are characteristic of the nature of an oil, fat, or wax, and assist most materially in identifying a given sample.

Besides these *constants* we have several "quantitative reactions" furnishing numbers that allow us to judge of the quality of a given oil or fat. These numbers will naturally vary with the state of purity, rancidity, age, etc. I therefore term these numbers "variables."[1]

The *constants* will be considered under the following heads :—

(1) The Saponification Value (Köttstorfer Value)—the measure of the amount of alkali requisite for neutralising the total fatty acids contained in a fat or wax.

(2) The (Bromine or) Iodine Value—the measure of the proportion of unsaturated fatty acids.

[1] *The Laboratory Companion to Fats and Oils Industries*, Macmillan, 1901, p. 6.

(3) The Reichert (or Reichert-Meissl) Value—the measure of the proportion of volatile fatty acids.
(4) The Hehner Value—the percentage of insoluble fatty matter, consisting of insoluble fatty acids + unsaponifiable matter.

The *variables* will comprise :—

(1) The Acid Value—a measure of the proportion of free fatty acids in a fat or wax.
(2) The amount of Glycerol, expressed in per cents.
(3) Diglycerides and Monoglycerides.
(4) The amount of Unsaponifiable Matter, expressed in per cents.

Midway between the two classes stands the *acetyl value*, which in some cases must be considered a "constant," whereas in other cases it is a "variable."

Besides the "quantitative reactions" we have a number of chemical reactions which are usefully applied to the examination of fatty substances, such as the elaïdin test, oxygen absorption test, hexabromide test, etc.

Hitherto these methods have not been worked out so fully as to admit of their being classed amongst the quantitative reactions, although in all probability at least some of them are likely to attain to that rank ; meanwhile we must look upon them as preliminary tests that can be usefully employed as sorting tests, or as confirmatory tests in those cases where the quantitative methods lead to ambiguous results. These preliminary tests or qualitative reactions will be described in the following chapter (chap. vii.).

Further insight into the composition of the natural oils, fats, and waxes is gained by examining the *isolated fatty acids*. The methods employed for this purpose will be dealt with in Chapter VIII.

The methods applied to the examination of the alcohols obtained on saponifying waxes, and in general to the unsaponifiable matter found in oils, fats, and waxes, as regards ascertaining their proportion and character, will be found in Chapter IX.

In this chapter only the *Quantitative Reactions* are considered.

QUANTITATIVE REACTIONS

A. CONSTANTS

1. The Saponification Value (Köttstorfer Value)

The saponification value (or Köttstorfer value) indicates the number of milligrams of potassium hydrate required for the complete saponification of one gram of a fat or wax ; or, in other words, *it represents the amount of potassium hydrate, expressed in tenths per cent, requisite to neutralise the total fatty acids in one gram of a fat or wax.*

For the determination of the saponification value are required—(1) An accurately standardised hydrochloric acid solution, the titer of which is expressed in terms of KOH; it is most convenient to use half-normal acid; (2) an alcoholic potash solution prepared by dissolving about 40 grms. of caustic potash, pure from alcohol, in a little water, and making it up with strong alcohol of specific gravity 0·810 or less to 1000 c.c. The alcoholic solution is allowed to stand for one day, and is then filtered through a large plaited filter into a bottle, conveniently closed by an india-rubber stopper fitted with a 25 c.c. pipette, the upper end of the pipette being closed in its turn by a short piece of india-rubber tubing and a clamp, or a glass rod. The bottle should be kept in an equably warm place; it need not be protected from light.

The alcohol used for preparing the potash solution should be as pure as possible. Commercial spirits of wine tested with a strong caustic potash solution should remain white; if it becomes yellow immediately, it must be rejected. If the alcohol has been pure, the alcoholic potash will not become brown even after several months' standing; it assumes, however, in course of time, a light yellow colouration, but this does not interfere with the accuracy of the titration.

Methylated spirit may be used in many cases, but it must be purified as described on p. 57. Since methylated spirit contains small quantities of mineral oils (added with the denaturing mixture), due care must be observed if the determination of the saponification value is combined with that of the unsaponifiable matter.

The determination of the saponification value is carried out as follows: Weigh off accurately, in a flask holding 150 to 200 c.c., 1·5 to 2 grms. of the purified and filtered fat. Next run into the flask *25 c.c. of the alcoholic potash, measuring it off by means of the* pipette fitted in the stopper of the bottle. It is not necessary to add exactly 25 c.c., but care must be taken that for each determination precisely the same quantity is used. A good plan is to allow the contents of the pipette to run out somewhat rapidly, and to drain it until two or three more drops have dropped off. Then attach a long cooling tube or an inverted condenser to the flask, and heat it on the boiling water-bath for half an hour so that the alcohol is kept simmering, frequently imparting to the contents of the flask a rotatory motion. Next add 1 c.c. of a 1 per cent phenolphthalein solution, and titrate back the excess of potash with the half-normal hydrochloric acid. In case too much alcohol has been volatilised, it is advisable to add some alcohol (previously neutralised), or to add normal acid at first and to finish the titration with half-normal acid.

It is always best to make a blank test, treating the same amount of alcoholic potash in exactly the same manner[1] as the solution of

[1] *This should extend as well to the material of the flask. Cheap German flasks are* attacked by the alkali to a considerable extent. It is best to use flasks made of Bohemian or Jena glass.

fat. Every source of error, as carbonic acid, etc., has therefore, as nearly as possible, in both tests the same influence on the final result, and is thus eliminated. The difference of the numbers of c.c. of acid used for the blank test and the real test corresponds to the quantity of potash required; this is calculated to milligrms. of potash for 1 grm. of fat.

Sulphuric acid should not be substituted for the hydrochloric acid, potassium sulphate being precipitated, whereby the delicacy of the end reaction is impaired.

For *Henriques'* method of cold saponification cp. p. 58.

In the case of dark-coloured solutions *McIlhiney*[1] proposes to measure the amount of alkali used, by the amount of ammonia it will liberate from an ammonium salt. He proceeds as follows: The substance (2 grms.) is saponified with excess of alcoholic caustic soda as usual, and the alcohol evaporated off. 250 c.c. of 93 per cent alcohol are added next, the soap dissolved by warming, and carbon dioxide passed through the solution for about one hour, in order to precipitate the excess of alkali as carbonate and bicarbonate. The precipitate is then filtered off, the alcohol evaporated from the filtrate, and 100 c.c. of a 10 per cent solution of ammonium chloride added, and heated, whereby the ammonia is distilled off. It is received in hydrochloric acid and titrated. A correction must, of course, be made for the sodium bicarbonate dissolved by the 93 per cent alcohol. This process is cumbersome and certainly introduces errors; it is far simpler to dilute the soap solution with sufficient alcohol, so as to obtain a distinct end reaction [or to employ as indicator alkali-blue (*De Negri* and *Fabris*)].

Example.—Weighed off 1·532 grms. of olive oil, and saponified with 25 c.c. of alcoholic potash solution. Required for titrating back 12·0 c.c. half-normal acid; further, required for the blank test 22·5 c.c. of the same acid. Therefore employed for saponification a quantity of caustic potash corresponding to

$$\frac{(22\cdot5 - 12\cdot0)\ 0\cdot0561}{2} \text{ grms.} = 294\cdot5 \text{ milligrms. KOH.}$$

Hence

$$\text{Used for 1 grm. of fat } \frac{294\cdot5}{1\cdot532} \text{ milligrms. KOH} = 192\cdot2 \text{ milligrms. KOH.}$$

The saponification value of the sample of olive oil is therefore 192·2.

Allen[2] proposed to calculate instead of the saponification value as defined here the *saponification equivalent*, this being the number of grams of fat saponified by one equivalent of potassium hydrate in grams, *i.e.* by 56·1 grms. KOH; or, what amounts to the same, by one litre of a normal solution of caustic potash or caustic soda. The saponification equivalent is found by dividing the percentage of potassium hydrate required for saponification into 5610.

There is no advantage gained by expressing this important value

[1] *Journ. Soc. Chem. Ind.* 1895. 197. [2] *Commercial Organic Analysis*, ii. 40.

in the manner proposed by *Allen*, and I shall therefore adhere to the saponification value as defined above, in order to avoid confusion The relation between the *saponification value* and *Allen's saponification equivalent* is shown by the following formulæ :—

$$\text{Sap. Val.} = \frac{\text{c.c. of normal potash} \times 56\cdot1}{\text{grms. of fat employed}} = \frac{\text{c.c. of normal potash} \times 56100}{\text{milligrms. of fat employed}}$$

$$\text{Sap. Equiv.} = \frac{5610}{\text{per cent KOH}} = \frac{5610}{\dfrac{\text{c.c. of normal potash} \times 0\cdot0561}{\text{grms. of fat employed}} \times 100}$$

$$= \frac{\text{grms. of fat employed} \times 5610}{\text{c.c. of normal potash} \times 5\cdot61} =$$

$$= \frac{\text{grms. of fat employed} \times 1000}{\text{c.c. of normal potash}} =$$

$$= \frac{\text{milligrms. of fat employed}}{\text{c.c. of normal potash}}$$

or, if a be the number of c.c. of normal potash, and b the number of milligrms. of fat employed :

$$\text{Sap. Val.} = \frac{a}{b} \times 56100 \text{ ; Sap. Equiv.} = \frac{b}{a}.$$

Hence it is clear that *Allen's* saponification equivalent can be found by dividing 56100 by the saponification value ; conversely, the saponification value is obtained by dividing 56100 by the saponification equivalent :

$$\text{Sap. Val.} = \frac{56100}{\text{Sap. Equiv.}} \text{ ; Sap. Equiv.} = \frac{56100}{\text{Sap. Val.}}$$

An easy calculation will show that saponification value and saponification equivalent are *identical* for the number $236\cdot87 = \sqrt{56100}$.

The saponification value of neutral glycerides and other esters of fatty acids varies, of course, with the nature of the fatty acids ; the lower the molecular weight of the fatty acids (or, what amounts to the same, of the esters) the more potash will be required to neutralise the fatty acids of 1 grm. of fat or wax, or, in other words, the higher will the saponification value be. To illustrate this more clearly, I subjoin in the following tables the saponification values of some pure triglycerides, diglycerides, monoglycerides, and also of some waxes (esters of monohydric alcohols).

[TABLE

Saponification Values of Triglycerides

	Formula.	Molecular Weight.	Saponific. Value.
Simple Triglycerides—			
Acetin	$C_3H_5(O . C_2H_3O)_3$	218	772·0
Butyrin	$C_3H_5(O . C_4H_7O)_3$	302	557·3
Valerin	$C_3H_5(O . C_5H_9O)_3$	344	489·2
Caproin	$C_3H_5(O . C_6H_{11}O)_3$	386	436·1
Caprylin	$C_3H_5(O . C_8H_{15}O)_3$	470	358·1
Caprin	$C_3H_5(O . C_{10}H_{19}O)_3$	554	303·7
Laurin	$C_3H_5(O . C_{12}H_{23}O)_3$	638	263·8
Myristin	$C_3H_5(O . C_{14}H_{27}O)_3$	722	233·1
Palmitin	$C_3H_5(O . C_{16}H_{31}O)_3$	806	208·8
Daturin	$C_3H_5(O . C_{17}H_{33}O)_3$	848	198·5
Stearin	$C_3H_5(O . C_{18}H_{35}O)_3$	890	189·1
Olein	$C_3H_5(O . C_{18}H_{33}O)_3$	884	190·4
Linolin	$C_3H_5(O . C_{18}H_{31}O)_3$	878	191·7
Linolenin	$C_3H_5(O . C_{18}H_{29}O)_3$	872	193·0
Ricinolein	$C_3H_5(O . C_{18}H_{33}O_2)_3$	932	180·6
Arachin	$C_3H_5(O . C_{20}H_{39}O)_3$	974	172·7
Erucin	$C_3H_5(O . C_{22}H_{41}O)_3$	1052	160·0
Cerotin	$C_3H_5(O . C_{26}H_{51}O)_3$	1226	137·3
Melissin	$C_3H_5(O . C_{30}H_{59}O)_3$	1394	120·7
Hydroxystearin . .	$C_3H_5(O . C_{18}H_{35}O_2)_3$	938	179·4
Dihydroxystearin .	$C_3H_5(O . C_{18}H_{35}O_3)_3$	986	170·7
Trihydroxystearin .	$C_3H_5(O . C_{18}H_{35}O_4)_3$	1034	162·8
Sativin	$C_3H_5(O . C_{18}H_{35}O_5)_3$	1082	155·0
Linusin	$C_3H_5(O . C_{18}H_{35}O_7)_3$	1178	142·4
Mixed Triglycerides—			
Acetodiformin . .	$C_3H_5(O . C_2H_3O)(O . COH)_2$	190	885·8
β-acetodibutyrin . .	$C_3H_5(O . C_4H_7O)(O . C_2H_3O)(O . C_4H_7O)$.	274	614·3
Myristopalmitoolein .	$C_3H_5(O . C_{14}H_{27}O)(O . C_{16}H_{31}O)(O . C_{18}H_{33}O)$	804	209·3
Oleodipalmitin . . (Dipalmitoolein) .	$C_3H_5(O . C_{16}H_{31}O)_2(O . C_{18}H_{33}O)$ . . .	832	202·3
Stearodipalmitin . . (Dipalmitostearin) .	$C_3H_5(O . C_{16}H_{31}O)_2(O . C_{18}H_{35}O)$ . . .	834	201·8
Oleodimargarin . . (Oleodidaturin) . .	$C_3H_5(O . C_{18}H_{33}O)(O . C_{17}H_{33}O)_2$ . . .	860	195·7
Oleopalmitostearin . (Stearopalmitoolein) .	$C_3H_5(O . C_{16}H_{31}O)(O . C_{18}H_{33}O)(O . C_{18}H_{35}O)$	860	195·7
Palmitodistearin . . (Distearopalmitin) .	$C_3H_5(O . C_{18}H_{35}O)_2(O . C_{16}H_{31}O)$ . . .	862	195·2
Daturodistearin . . (Distearodaturin) .	$C_3H_5(O . C_{17}H_{33}O)(O . C_{18}H_{35}O)_2$ . .	876	192·1
Oleodistearin . .	$C_3H_5(O . C_{18}H_{33}O)(O . C_{18}H_{35}O)_2$ . .	888	189·5
Elaïdodistearin . ..	$C_3H_5(O . C_{18}H_{33}O)(O . C_{18}H_{35}O)_2$ . .	888	189·5
Dioleostearin . .	$C_3H_5(O . C_{18}H_{33}O)_2(O . C_{18}H_{35}O)$ . . .	886	189·9

[TABLE

Saponification Values of Diglycerides

Diglyceride.	Formula.	Molecular Weight.	Saponification Value.
Diacetin	$C_3H_5(OH)(O.C_2H_3O)_2$	176	637·6
Dibutyrin	$C_3H_5(OH)(O.C_4H_7O)_2$	232	483·7
Divalerin	$C_3H_5(OH)(O.C_5H_9O)_2$	*260*	431·5
Dicaproin	$C_3H_5(OH)(O.C_6H_{11}O)_2$	288	389·6
Dicaprylin	$C_3H_5(OH)(O.C_8H_{15}O)_2$	344	326·2
Dicaprin	$C_3H_5(OH)(O.C_{10}H_{19}O)_2$	400	280·5
Dilaurin	$C_3H_5(OH)(O.C_{12}H_{23}O)_2$	456	246·1
Dimyristin	$C_3H_5(OH)(O.C_{14}H_{27}O)_2$	512	219·1
Dipalmitin	$C_3H_5(OH)(O.C_{16}H_{31}O)_2$	568	197·6
Didaturin	$C_3H_5(OH)(O.C_{17}H_{33}O)_2$	596	188·3
Distearin	$C_3H_5(OH)(O.C_{18}H_{35}O)_2$	624	179·8
Diolein	$C_3H_5(OH)(O.C_{18}H_{33}O)_2$	620	181·0
Dilinolin	$C_3H_5(OH)(O.C_{18}H_{31}O)_2$	616	182·1
Dilinolenin	$C_3H_5(OH)(O.C_{18}H_{29}O)_2$	612	183·3
Diricinolein	$C_3H_5(OH)(O.C_{18}H_{33}O_2)_2$	652	172·1
Diarachin	$C_3H_5(OH)(O.C_{20}H_{39}O)_2$	680	165·0
Dierucin	$C_3H_5(OH)(O.C_{22}H_{41}O)_2$	732	153·3
Dicerotin	$C_3H_5(OH)(O.C_{26}H_{51}O)_2$	848	132·3
Dimelissin	$C_3H_5(OH)(O.C_{30}H_{59}O)_2$	940	119·1
Dihydroxystearin	$C_3H_5(OH)(O.C_{18}H_{35}O_2)_2$	656	171·1
Didihydroxystearin	$C_3H_5(OH)(O.C_{18}H_{35}O_3)_2$	688	163·1
Ditrihydroxystearin	$C_3H_5(OH)(O.C_{18}H_{35}O_4)_2$	720	155·9
Disativin	$C_3H_5(OH)(O.C_{18}H_{35}O_5)_2$	752	149·2
Dilinusin	$C_3H_5(OH)(O.C_{18}H_{35}O_7)_2$	816	137·5
Of Acid Mol. Wt. = 276	$C_3H_5(OH)(O.R)_2(R=250)$	608	184·5

Saponification Values of Monoglycerides

Monoglyceride.	Formula.	Molecular Weight.	Saponific. Value.
Monoacetin	$C_3H_5(OH)_2(O.C_2H_3O)$	134	428·7
Monobutyrin	$C_3H_5(OH)_2(O.C_4H_7O)$	162	346·3
Monovalerin	$C_3H_5(OH)_2(O.C_5H_9O)$	*176*	*318·8*
Monocaproin	$C_3H_5(OH)_2(O.C_6H_{11}O)$	190	295·3
Monocaprylin	$C_3H_5(OH)_2(O.C_8H_{15}O)$	218	257·3
Monocaprin	$C_3H_5(OH)_2(O.C_{10}H_{19}O)$	246	228·1
Monolaurin	$C_3H_5(OH)_2(O.C_{12}H_{23}O)$	274	204·7
Monomyristin	$C_3H_5(OH)_2(O.C_{14}H_{27}O)$	302	185·8
Monopalmitin	$C_3H_5(OH)_2(O.C_{16}H_{31}O)$	330	170·0
Monodaturin	$C_3H_5(OH)_2(O.C_{17}H_{33}O)$	344	163·1
Monostearin	$C_3H_5(OH)_2(O.C_{18}H_{35}O)$	358	156·7
Monoolein	$C_3H_5(OH)_2(O.C_{18}H_{33}O)$	356	157·58
Monolinolin	$C_3H_5(OH)_2(O.C_{18}H_{31}O)$	354	158·5
Monolinolenin	$C_3H_5(OH)_2(O.C_{18}H_{29}O)$	352	159·4
Monoricinolein	$C_3H_5(OH)_2(O.C_{18}H_{33}O_2)$	372	150·9
Monoarachin	$C_3H_5(OH)_2(O.C_{20}H_{39}O)$	386	145·3
Monoerucin	$C_3H_5(OH)_2(O.C_{22}H_{41}O)$	412	136·2
Monocerotin	$C_3H_5(OH)_2(O.C_{26}H_{51}O)$	470	119·3
Monomelissin	$C_3H_5(OH)_2(O.C_{30}H_{59}O)$	526	106·6
Monohydroxystearin	$C_3H_5(OH)_2(O.C_{18}H_{35}O_2)$	374	150·0
Monodihydroxystearin	$C_3H_5(OH)_2(O.C_{18}H_{35}O_3)$	390	143·9
Monotrihydroxystearin	$C_3H_5(OH)_2(O.C_{18}H_{35}O_4)$	406	138·2
Monosativin	$C_3H_5(OH)_2(O.C_{18}H_{35}O_5)$	422	133·0
Monolinusin	$C_3H_5(OH)_2(O.C_{18}H_{35}O_7)$	454	123·6
Of Acid Mol. Wt. = 276	$C_3H_5(OH)_2(OR)(R=259)$	350	160·3

Saponification Values of Waxes

Wax.	Formula.	Molecular Weight.	Saponific. Value.
Cetyl palmitate, cetin . .	$C_{16}H_{33} . O . CO . C_{15}H_{31}$	480	116·9
Octodecyl palmitate . . .	$C_{18}H_{37} . O . CO . C_{15}H_{31}$	508	110·4
Ceryl palmitate	$C_{26}H_{53} . O . CO . C_{15}H_{31}$	620	90·5
Myricyl palmitate, myricin .	$C_{30}H_{61} . O . CO . C_{15}H_{31}$	676	83·0
Cetyl stearate	$C_{16}H_{33} . O . CO . C_{17}H_{35}$	508	110·4
Ceryl cerotate	$C_{26}H_{53} . O . CO . C_{25}H_{51}$	760	73·8
Coceeryl coccerate, coccerin .	$C_{30}H_{60} . (O . C_{31}H_{61} . O_2)_2$	1382	81·2
Cholesteryl palmitate . .	$C_{26}H_{43} . O . CO . C_{15}H_{31}$	610	92·0
Cholesteryl oleate . . .	$C_{26}H_{43} . O . CO . C_{17}H_{33}$	636	88·2
Cholesteryl stearate . . .	$C_{26}H_{43} . O . CO . C_{17}H_{35}$	638	87·9
Isocholesteryl stearate . .	$C_{26}H_{43} . O . CO . C_{17}H_{35}$	638	87·9
Cholesteryl cerotate . . .	$C_{26}H_{43} . O . CO . C_{25}H_{51}$	750	74·8
Myricyl melissate . . .	$C_{30}H_{61} . O . CO . C_{29}H_{59}$	872	64·3
Psyllostearyl psyllostearylate .	$C_{33}H_{67} . O . CO . C_{32}H_{65}$	956	58·6

The preceding tables refer to neutral substances only, that is, to glycerides and waxes free from fatty acids.

Since the natural oils, fats, and waxes contain certain amounts of free fatty acids, depending on the state of purity of the individual oil, fat, or wax, it cannot be expected that different samples of one and the same kind of oil, fat, or wax will always have the same saponification values. Although the saponification values are very characteristic numbers, as the following table shows, they cannot be considered, in the strictest sense of the word, as constants. For, in the first instance, certain fluctuations must occur, depending on the proportion of free fatty acids. These fluctuations will be small since, to take an example, the amount of caustic potash required to saponify 100 parts of stearin differs by only 5 per cent from the amount of caustic potash required to neutralise 100 parts of stearic acid. This is clearly brought out by the following table:—

Variation of Saponification Value with the Amount of Free Fatty Acids

Stearin. Per cent.	Stearic Acid. Per cent.	Saponification Value.	Neutralisation Value.
100	0	189·1	0
75	25	191·02	49·37
50	50	193·30	98·75
25	75	195·41	148·13
0	100	197·5	197·5

Besides the proportion of free fatty acids, such natural conditions as climate, difference of soil, seem to cause some variations of the saponification value.

Notwithstanding these disturbing influences, the saponification numbers are fairly constant, and constitute, therefore, an important

test in determining the nature of an oil or fat. In the following table I have collated the mean values from a large number of observations of the oils, fats, and waxes examined hitherto. The several observations from which the means have been deduced will be found under the heads of the individual oils, fats, and waxes in Chapter XIV. The numbers have been arranged according to the system which I have adopted in this work.

Saponification Values of Oils, Fats, and Waxes

Oil.	Class.	Group.	Saponification Value.
Perilla	Drying oils		189·6
Linseed			192-195
Tung oil			193
Lallemantia			185
Candle nut			192·6
Stillingia			210·4
White acacia			192·4
Cedar nut			191·8
Garden rocket			191·8
Hemp seed			192·5
Walnut, nut			195
Safflower			186·6-193·3
Echinops oil			189·2-190
Poppy seed			195
Henbane			170·8
Amoora			189·7
Niger seed			190·2
Sunflower			193·5
Asparagus seed			194·1
Celosia			190·5
Yellow acacia			190·6
Para rubber tree seed			206·1
Argemone			187·3-190·3
Fir seed			191·3
Madia			192·8
Indian laurel			170
Cameline	Semi-drying oils	Cotton seed oil group	188
Clover oil, red ; white			189·9 ; 189·5
Soja bean			192·7
Daphne			196·5
Pumpkin seed			188·4
Water melon			189·7
Maize (corn)			188-193
Wheat			187-190
Beech nut			191-196
Datura			186
Basswood			178·1
Kapok			181-196·5
Cotton seed			*193-195*
Sesamé			189-193
Lemon pips			188·4
Luffa seed			187·8
Brazil nut			193·4
Croton			210-215
Curcas, purging nut			193·2

Saponification Values of Oils, Fats, and Waxes—continued

Oil.	Class	Group.	Saponification Value.
Sorghum	Semi-drying oils	Cotton seed oil group	172·1 (?)
Coumou			169·1
Pinot			162·4 (?)
Garden cress		Rape oil group	178-183
Ravison			174-179
Hedge mustard			174
Rape (colza)			170-179
Black mustard			174
White mustard			170-174
Radish seed			173-178
Jamba			172·3
Small fennel	Non-drying oils		196·4
Quince			181·8
Cherry kernel			193-195
Cherry laurel			194
Apricot kernel			192·5
Plum kernel			191·5
Peach kernel			192·5
Almond			191·0
Sanguinella			192·1
Wheat meal			166·5 (?)
Acorn			199·3
Californian nutmeg			191·3
Arachis			190-196
Rice			193·2
Tea seed (Chinese			195·5
Tea seed (Assam)			194·0
Pistachio			191·3
Hazel nut			192·0
Koëme			174·8 (?)
Elderberry			209·3
Birch seed			211
Olive			185-196
Olive kernel			183
Coffee berry			173-177
Ungnadia			191·5
Strophantus			187·9
Paradise nut			173·6
Secale			178·4
Grape seed		Castor oil group	178·5
Castor			183-186
Menhaden	Marine animal oils	Fish oils	190·6
Japanese sardine			189·8-192·1
Salmon			182·8
Herring			171-194
Sturgeon			186·3
Cramp fish			148·2 (?)
Sunfish			147·6 (?)

Saponification Values of Oils, Fats, and Waxes—continued

Oil.	Class.	Group.	Saponification Value.
Cod liver	Marine animal oils	Liver oils	171-189
Haddock liver			188·8
Skate liver			185·4
Shark liver			161·0
Coal fish liver			177-181
Ling			184·1
Seal		Blubber oils	189-196
Whale			188·0
Turtle			209
Dugong			197·5
Dolphin (body)			197·3
Dolphin (jaw)			290
Porpoise (body)			195
Porpoise (jaw)			254-272
Sheep's foot	Terrestrial animal oils		194·7
Horses' foot			195·9
Neat's foot			194·3
Egg			184·4-190·2
Pongam	Vegetable fats		178-183·1
Chaulmoogra			204
Laurel			197·9
Carapa			195·6
Margosa			196·9
Kodam seed			197·6
Mahua butter			190-194
Mowrah seed			188-192
Shea butter			179-192
Palm oil			196-202
Akee oil			194·6
Macassar			221·5
Sawarri			199·51
Mafura tallow			200-221
Nutmeg butter			154-191
Phulwara butter			190·8
Mkanyi fat			190·5
Rambutan tallow			193·8
Malabar tallow			188·7-192
Cacao butter			193·55
Vegetable tallow			200·3
Kokum butter			187-191
Muriti fat		Cocoa nut oil group	246·2
Mocaya oil			240·6
Cohune			219·4-220·5
Maripa			270·5
Palm nut oil			242-250
Cocoa nut oil			246-260
Cocos acrocomoides			292·8

Saponification Values of Oils, Fats, and Waxes—continued

Fat.	Class.	Group.	Saponification Value.
Ucuhuba	Vegetable fats		219·5
Japan wax			217-237·5
Myrtle wax			208·7
Icebear	Animal fats	Drying fats	187·9
Blackcock			201·6
Hare			200·9
Rabbit (wild)			199·3
Rabbit (tame)		Non-drying fats	202·6
Wild duck			198·5
Starling			209·2
Turkey			200·5
Fox			191·7
Horse			195-197
Horse marrow			199·8
Badger			193·1
Pine marten			204
Goose (domestic)			193·1
Goose (wild)			196
Chicken			193·5
Human, adult			195
Lard			195·4
Fat from wild boar			195·1
Dog			195·4
Wild cat			199·9
Domestic cat			190·7
Beef marrow			199
Bone			190·9
Beef tallow			193·2-200
Mutton tallow			192-195·2
Butter			227
Elk			195·1
Reindeer			194·7
Roebuck			199·0
Fallow buck			195·6
Chamois			203·3
Stag			199·9
Sperm oil	Liquid waxes		125·2-132·6
Arctic sperm oil			123-135·9
Carnaüba wax	Solid waxes	Vegetable waxes	79-95
Pisang wax			109
Flax wax			101·5
Wool wax		Animal waxes	102·4
Beeswax			90-98
Spermaceti			123-135
Insect wax			80·5-93

In the first instance, it will be noted that the waxes are characterised by such low saponification values, that these numbers alone afford a ready means of differentiating waxes from oils and fats.

It will further be seen that the majority of oils and fats have a saponification value lying in the neighbourhood of 193. In the case of an unknown sample, wide deviations from this number in either direction will at once enable the analyst to single out individual oils.

Thus, oils belonging to the rape oil group are characterised by a considerably lower saponification value, namely, about 175. The lower saponification values of these oils are explained by the large proportion of erucin they contain. Similarly, grape seed oil and castor seed oil may be differentiated from the bulk of the other oils by their lower saponification values. In the case of castor oil, the lower value is due to the presence of hydroxylated fatty acids.

On the other hand, large deviations in the opposite direction enable us to single out a number of oils and fats, and hence render their recognition a comparatively easy task. Thus the high saponification values of the fluid portion of dolphin and porpoise oils are indicative of a high proportion of lower fatty acids. A prominent example of a characteristically high saponification value is butter fat, so that by the saponification value alone, butter fat can be differentiated from margarine. High saponification values, due to the large proportion of glycerides of lower fatty acids, are also characteristic of the oils of the cocoa nut oil group.

It should be noted that the above remarks regarding the indications furnished by the saponification value refer to unadulterated oils, fats, and waxes, *i.e.* to commercial samples which may contain a smaller or larger amount of free fatty acids, and also small amounts of unsaponifiable matter. If mineral oils or other unsaponifiable substances are intermixed with the fatty substances, then naturally the saponification values alone, if considered without further investigation, would be entirely misleading, since the unsaponifiable matters naturally depress the saponification value. Thus, to take an example, an oil having the saponification value 193, if adulterated with 10 per cent of mineral oil, would show a saponification value of about 175, and might, therefore, be mistaken for a rape oil if no further tests were applied.

Again, if colophony (rosin) is dissolved in the fatty substance, the saponification value will be thereby unaffected, if rosin of about the same saponification value be used; if a rosin of somewhat lower saponification value be used, the saponification value will thereby be somewhat depressed.

2. The (Bromine or) Iodine Value

The (bromine or) iodine value indicates the percentage of (bromine or) iodine chloride absorbed by a fat or wax, expressed in terms of (bromine or) iodine.

This value is a measure of the proportion of unsaturated fatty acids, these acids, both in their free state and in combination with glycerol, having the property of assimilating the halogens with formation of additive compounds.

Theoretically, the acids belonging to the oleic and ricinoleic series should absorb two atoms of chlorine, bromine, or iodine. Hence the glycerides of these acids should absorb six atoms of iodine. Similarly the acids of the linolic series should assimilate four atoms, the members of the linolenic series six atoms of the halogens, etc.

Obviously the determination of absorbed chlorine is attended with more difficulty than that of bromine or iodine; hence in technical analysis only bromine and iodine—the latter in the form of iodine chloride—are being employed.

Bromine Value

If dry bromine is allowed to act on an oil, it is absorbed with a more or less violent reaction, and evolution of hydrobromic acid takes place. The reaction must therefore be moderated by previously dissolving both the bromine and the oil in a suitable solvent.

The determination of **bromine absorption** values was proposed by *Cailletet* (1857); the application of this method for the analysis of fats is, however, due to *Mills*[1] and his collaborators *Snodgrass* and *Akitt*.

Mills proceeds as follows:—0·1 grm. of a fat, dried thoroughly and filtered, is dissolved in 50 c.c. of carbon tetrachloride contained in a narrow-mouthed stoppered bottle of 100 c.c. capacity. To this solution is added a standard carbon tetrachloride solution of bromine (about 0·006-0·008 grms. per c.c.) until after the lapse of fifteen minutes the colouration persists. The excess of bromine can be measured either by comparing the colouration with that similarly produced in a blank experiment, or, more accurately, by titrating back with a standard solution of β-naphthol in carbon tetrachloride, when monobromnaphthol is formed. The bromine absorbed is calculated for 100 grms. of fat. The average probable error is stated to be 0·46 per cent.

Mills laid the greatest stress on the necessity of rigidly excluding moisture, since he observed that the bromine absorption number increased in presence of water; therefore aqueous solutions of bromine must not be used. Carbon tetrachloride was substituted for carbon bisulphide, for the reason that the solution of bromine in the former possesses much greater stability at the ordinary temperature than in the latter.[2] Instead of β-naphthol, potassium iodide may be added, and the liberated iodine titrated with sodium thiosulphate, calculating it to bromine.

Small quantities of hydrobromic acid are formed during the

[1] *Journ. Soc. Chem. Ind.* 1883, 435; 1884, 366.

[2] The following reaction going on in a solution of bromine in carbon bisulphide should be noted as involving loss of bromine. After several days' standing CS_2Br_4 is formed; this is decomposed by water (moisture) with separation of crystals of $(CBr_3)_2S_3$.—(J. L.)

process. These are not due to any moisture, but to the substitution of hydrogen in the molecule of the fatty substance. (The hydrobromic acid thus formed can be detected by shaking the product with water and testing the aqueous solution with silver nitrate.)

Thus concurrently with the **addition**, *i.e.* the absorption of bromine due to two or more atoms of bromine being assimilated by one molecule of an unsaturated glyceride to form a saturated compound, a further quantity of free bromine disappears owing to the formation of substitution products and consequently of hydrobromic acid; therefore the **total absorption** of bromine, as measured by the method just described, is due to both **addition** and **substitution**.

The more concentrated the bromine solution employed, the greater will be the amount of substitution products; it is therefore evident that bromine values obtained by allowing dry bromine to act on an oil, are likely to come out too high.

A measure of the amount of substitution that has taken place is furnished by the quantity of hydrobromic acid formed. Hence the **true bromine value** is found from the difference between the total bromine assimilated and the bromine absorbed by substitution.

McIlhiney[1] determines the "bromine addition" and the "bromine substitution" value of an oil in the following manner:[2]—

From 0·25 to 1·00 grm. of the sample is dissolved in 10 c.c. of carbon tetrachloride in a 500 c.c. stoppered bottle, and an excess of a $\frac{1}{3}$ normal solution of bromine in carbon tetrachloride is added. After a few minutes the bottle is placed in ice so that a partial vacuum is produced by the condensation of the vapours. A piece of india-rubber tubing is now slipped over the neck so as to form a well around the stopper. The well is filled with water, which is sucked into the bottle when the stopper is carefully lifted. 25 c.c. of water are introduced into the bottle, its contents are well shaken, to effect absorption of the hydrobromic acid, and 10-20 c.c. of a 20 per cent solution of potassium iodide and about 75 c.c. more water are added. The iodine liberated by the excess of bromine is measured by titration with standard thiosulphate solution and calculated to bromine. The total amount of bromine added *having been ascertained similarly in a blank test, the difference* between the two amounts corresponds to the **total bromine absorption**; this is calculated to units per cent of the sample taken.

The contents of the bottle are next transferred to a separating funnel, and the aqueous solution is separated and filtered. If it be blue it is decolourised by a few drops of thiosulphate solution, and the free acid determined as hydrobromic acid by titration with decinormal alkali, methylorange being used as an indicator.[3] The bromine calculated from the hydrobromic acid and expressed in per cents of the sample gives the **bromine substitution value**. Twice this number subtracted from the total bromine absorption gives the **bromine addition number.**

[1] *Journ. Soc. Chem. Ind.* 1894, 668. [2] Cp. Allen, *Commercial Organic Analysis*, ii. 384.
[3] For another method cp. McIlhiney, *Journ. Amer. Chem. Soc.* 1899, 1084.

It is obvious that the substitution number must be doubled, since for each bromine atom that has been converted into hydrobromic acid, there has been removed from the original bromine solution 1 molecule (or 2 atoms) of bromine, as explained by the following equation :—

$$\underset{\text{Fatty Acid.}}{C_nH_mO_2} + Br_2 = \underset{\text{Bromosubstitution product.}}{C_nH_{m-1}O_2Br} + HBr.$$

The following *gravimetric* process for the determination of the bromine value has been proposed by *Hehner* :[1]—Weigh off accurately 1 to 3 grms. of the oil in a wide-mouthed flask, and dissolve it in a few cubic centimetres of chloroform. Then add pure bromine, drop by drop, until there is an excess of bromine. Heat the flask on the water-bath until the bulk of the bromine is driven off, add a little more chloroform, and heat again so as to promote the evaporation of the bromine by the vapours of the chloroform. This operation may be repeated so as to ensure complete volatilisation of the bromine in excess. The contents of the flask are finally heated at 125° C. until the weight remains constant. This takes several hours, a little acroleïn and hydrobromic acid escaping during the drying. The gain in weight expressed in per cents gives the bromine value. Essentially the same method has been described, independently, by *Waller*.[2] *Lewkowitsch*,[3] however, has shown that whilst in a number of cases (*e.g.* olive oil) this method leads to results agreeing with those obtained by *Hübl's* standard method (see below), in other cases such enormous discrepancies are observed that this gravimetric method cannot be recommended.[4]

The determination of the bromine value has been wholly superseded by *Hübl's* method of ascertaining the **iodine absorption** value, which yields far more constant and reliable results.[5] In fact, the reliability of the bromine absorption processes is ascertained by their agreement with *Hübl's* process, bromine values being calculated to iodine values by multiplication with $\frac{127}{80} = 1{\cdot}5875$.

But it should be distinctly understood that the bromine values are not directly convertible into iodine values, since a varying amount of substitution takes place concurrently with absorption, as pointed out already. Therefore, the bromine absorption method will be resorted to in exceptional cases only, such as in that of rosin oils (chap. xv.) or linseed and boiled oils suspected of being adulterated with rosin oils.

The bromine absorption method has found useful application in the hexabromide test (chaps. vii. and viii.).

[1] *Analyst*, 1895, 50.
[2] *Ibid.* 1895, 280. It should be noted that *Waller* examined olive oil only.
[3] *Journ. Soc. Chem. Ind.* 1896, 859.
[4] Cp. also Jenkins, *Journ. Soc. Chem. Ind.* 1897, 193.
[5] Hydroxybrassidic acid does not absorb bromine at the ordinary temperature (*Berichte*, 26, 839).

Hübl[1] found that iodine is only slowly assimilated by fats at the ordinary temperature, whilst at higher temperatures[2] the action of iodine becomes very irregular, complicated reactions taking place. He has ascertained, however, that from an alcoholic solution of iodine, in presence of mercury bichloride, glycerides of the unsaturated fatty acids absorb iodine in a very regular, well-defined manner, so that a quantitative method may be based on this reaction. The following solutions are required for **Hübl's process**:—

1. *Solution of Iodine and Mercury Bichloride*, called hereafter *Iodine Solution* (for brevity).—This is prepared by dissolving on the one hand 25 grms. of iodine in 500 c.c. of pure 95 per cent alcohol, and on the other hand 30 grms. of mercury bichloride in the same amount of 95 per cent alcohol (filtering the latter solution if necessary), and then mixing both solutions. The iodine solution undergoes considerable reduction in strength (*i.e.* free iodine) during the first hours after mixing, and should, therefore, be allowed to stand for twelve to twenty-four hours before use. It is not advisable to use iodine solutions older than twenty-four hours. Even after that time the iodine solution gradually loses strength and is apt to lead to uncertain results. The writer finds it convenient to keep both the iodine and the bichloride solutions in stock separately, and prepare only so much *iodine solution* as is required for a test.

2. *Solution of Sodium Thiosulphate* (hyposulphite).—This is prepared by dissolving about 24 grms. of the crystallised salt in 1000 c.c. of water, and is standardised by means of iodine in the following manner:—Two short glass tubes, sealed at one end, and of such dimensions that one fits with slight friction into the other, are heated and allowed to cool in the desiccator. Now transfer to the inner tube about 0·2 grm. of pure resublimed iodine, lay the tube obliquely in a sand-bath, heat till the iodine melts, then remove the tube, and allow it to cool a little in an oblique position, until it can be held with the hand. Place the larger tube over it, allow to cool in the desiccator, and weigh accurately. Then take the wider tube off, and place both tubes in a stoppered bottle containing 1 grm. of potassium iodide dissolved in 10 c.c. of water. As soon as the iodine is dissolved, add water, and allow the thiosulphate to run into it from a burette until the colour is nearly all gone. Now add a little starch solution, and then carefully, with constant agitation, drop by drop of the thiosulphate until the blue colour just disappears.

Another very convenient method for standardising the thiosulphate, due to *Volhard*, is the following:—Weigh off accurately 3·8774[3] grms. of pure potassium bichromate,[4] and dissolve in 1000 c.c. of water. Place in a stoppered bottle 10 c.c. of a 10 per cent potassium iodide solution, and 5 c.c. of hydrochloric acid, and run in exactly 20 c.c. of the bichromate solution from a burette. Since

[1] *Journ. Soc. Chem. Ind.* 1884, 641.
[2] *Ibid.* 1894, 616 (Schweitzer and Lungwitz).
[3] O=16.
[4] It is necessary to ascertain its purity and absence of sodium bichromate by determining its oxidising value.

each c.c. of this solution liberates precisely 0·01 grm. of iodine, altogether 0·2 grm. of iodine will be set free. This is titrated by means of the thiosulphate solution as described above. The advantage of this method lies in its rapidity, saving the somewhat laborious and circumstantial preparation and weighing off of the pure iodine; besides, the bichromate solution, keeping for an indefinite time without alteration, is always ready for ascertaining the strength of the thiosulphate solution.[1]

3. *Chloroform.*—The chloroform should be pure. It is tested by mixing 10 c.c. with 10 c.c. of the iodine solution, and titrating the free iodine after two or three hours' standing. The amount found should be exactly the same as that contained in 10 c.c. of the iodine solution. (Ether cannot be used in place of chloroform, as it very frequently contains hydrogen peroxide, which acts on potassium iodide, liberating iodine. Carbon tetrachloride, also benzene, *free from thiophene*,[2] are suitable substitutes for chloroform.)

4. *Solution of Potassium Iodide.*—This is prepared by dissolving 100 grms. of potassium iodide in 1000 c.c. of water. Commercial potassium iodide frequently contains iodate, which gives free iodine with hydrochloric acid. Such impure iodide may, however, be employed if accurately measured volumes be used and the liberated iodine be taken into account.

5. *Starch Solution.*—This should be prepared afresh for each analysis by stirring 0·5 grm. of pure starch in 50 c.c. of cold water, and heating to the boiling point with constant stirring.

The determination of the iodine value is carried out as follows:—From 0·15 to 0·18 grm. of a drying, or a marine animal oil, 0·2 to 0·3 grm. of a semi-drying oil, 0·3 to 0·4 grm. of a non-drying oil, or 0·8 to 1·0 grm. of a solid fat, are weighed off accurately, and placed in a bottle of 500 to 800 c.c. capacity provided with a well-ground stopper. The fat is dissolved in 10 c.c. of chloroform, and 25 c.c. of the iodine solution run in by means of a pipette inserted in the reagent bottle. The pipette is always emptied in exactly the same manner: this is best done by allowing it to drain until two or three drops have run out. For larger quantities of fats, say 0·30 to 0·36 grm., etc., 50 c.c. must be used. In order to prevent loss of iodine by volatilisation it is advisable to moisten the stopper with potassium iodide solution. The chloroform and iodine solution should give a clear solution on shaking, otherwise more chloroform must be added. The bottle is then allowed to stand in a dark place. Should the deep brown colour of the solution disappear after a short time, another 25 c.c. of the iodine solution must be run in, an excess of iodine being required for the reaction. The solution must, after two hours, still possess a deep brown colour. Most of the iodine is absorbed during these first two hours. The reaction then slows down and cannot be considered completed before six to eight hours in the

[1] For a method of standardising by means of BaS_2O_3, cp. Plumpton and Chorley, *Proc. Chem. Soc.* 1895, p. 38.

[2] Farnsteiner, *Zeit. f. Unters. der Nahrgs. u. Genussmittel*, 1898, 529.

case of solid fats and non-drying oils, and twelve to eighteen hours in the case of drying oils and fish oils. Semi-drying oils require eight to ten hours to complete the absorption of iodine. After standing for the requisite number of hours, from 15 to 20 c.c. of the potassium iodide solution are run in, and the liquid shaken and diluted with from 300 to 500 c.c. of water.[1] A red precipitate of mercury iodide would indicate that an insufficient quantity of potassium iodide had been employed, and therefore more must be added. The excess of free iodine, part of which will be in the aqueous solution, whereas the remainder is dissolved in the chloroform, is titrated with the thiosulphate solution by running it into the bottle until after repeated agitation, both the aqueous and the chloroformic layers are but faintly coloured. A few drops of the starch solution are next added and the titration brought to an end. Immediately before or after this test 25 c.c. of the original iodine solution are standardised in exactly the same manner. The difference between the two results corresponds to the assimilated halogen, and is calculated in terms of iodine to units per cent of the sample. The figure thus found is termed the **iodine value**.

The values as obtained by *Hübl's* method are quite constant, provided an excess of iodine of not less than the amount actually absorbed has been employed, and the operations be always carried out under identical conditions. The results do not depend on the concentration, nor on an excess of the mercury bichloride solution, but it is necessary that for every two atoms of iodine at least one molecule of mercury bichloride should be present.

When the titrated solution is allowed to stand for some time the solution becomes blue again; this is no doubt due to the splitting off of iodine, thus proving that the action of iodine on unsaturated compounds is to some extent a reversible one. However, this action does not in the least interfere with the accuracy of the titration.

Example.—Weighed off 0·3394 grm. of lard, dissolved in 10 c.c. carbon tetrachloride, added 25 c.c. of iodine solution, which required in a blank experiment 60·9 c.c. of thiosulphate solution, 16·45 c.c. of which were equivalent to 0·2 grm. of iodine. For titrating back the excess of iodine in the experiment there were required 39·6 c.c. thiosulphate solution. Hence, the iodine absorbed corresponds to $60{\cdot}9 - 39{\cdot}6 = 21{\cdot}3$ c.c. thiosulphate solution.

Since 16·45 c.c. of thiosulphate solution are equivalent to 0·2 grm. of iodine, 21·3 c.c. correspond to $\frac{0{\cdot}2 \times 21{\cdot}3}{16{\cdot}45} = 0{\cdot}2589$ grm. of iodine. Hence 0·3394 grm. of lard absorbed 0·2589 grm. of iodine, or 100 grms. absorbed $\frac{0{\cdot}2589 \times 100}{0{\cdot}3394} = 76{\cdot}28$ grms. of iodine. The iodine value of the lard is therefore 76·28.

Hübl's process has been examined by many chemists, and proved itself to be one of the most valuable methods employed in the technical analysis of fats and waxes. The chemical literature of the

[1] Cp. Ingle, *Journ. Soc. Chem. Ind.* 1902, 587, and Harvey, *Ibid.* 1902, 1438.

last decade contains numerous papers by various authors purporting to give improvements or modifications of the original method. Most of them refer simply to minor or unimportant points. Some of them even reproduce methods which *Hübl*, in his classic paper, has rejected. With the exception of the important *Wijs'* modification (described below) they are omitted here, and the reader must be referred for a short survey of the earlier literature of this subject to the last edition of this work.

It need only be stated that long before a comprehensive explanation of the reactions taking place in *Hübl's* ingenious process was found, the numbers obtained by this process were such as afforded the most valuable guidance in the examination of oils and fats. *Hübl* himself explained the reaction by assuming that a chloro-iodo-addition compound was formed, he having obtained from oleic acid a fatty substance, to which he ascribed the formula $C_{18}H_{34}ClIO_2$.

If *Hübl's* view is correct, then theory requires, in the first instance, that saturated fatty acids should have no iodine value; secondly, that pure unsaturated fatty acids should furnish iodine values agreeing with the theoretical numbers.

As regards the first point, I have examined a number of pure saturated fatty acids, and also amyl alcohol, with the following result:—

	Iodine Value (100 grms. absorb grms. Iodine).
Propionic acid	0·66
Butyric ,,	0·36
Isobutyric ,,	0·00
Valeric ,,	1·32
Caproic ,,	0·30
Œnanthic ,,	0·00
Caprylic ,,	0·55
Pelargonic ,,	1·83
Capric ,,	0·31
Lauric ,,	1·12
Palmitic ,,	0·13
Stearic ,,	0·20
Cerotic ,,	1·34
Amyl alcohol	0·00

The iodine values should, of course, have been in all cases *nil*, but considering the difficulty of satisfactorily purifying the fatty acids, the results may be accepted as proving the fact that saturated fatty acids have no iodine value.

The second postulate has been borne out by the experiments set out in the following table:—

[TABLE

Fatty Acid.	Formula.	Atoms of Iodine required to form a saturated Compound.	100 Grms. of Acid absorb Iodine.		Observer.
			Theory.	Experiment.	
			Grms.	Grms.	
Oleic . .	$C_{18}H_{34}O_2$	2	90·07	89	Geitel[1]
Elaidic . .	$C_{18}H_{34}O_2$	2	90·07	90·54	Saytzeff[2]
Brassidic .	$C_{22}H_{42}O_2$	2	75·15	75·34	„ [3]
Isoerucic .	$C_{22}H_{42}O_2$	2	75·15	74·42	Alexandroff and Saytzeff[4]

Although the writer found in the case of crotonic acid, fumaric acid, maleïc acid, cinnamic acid, and styracin, that these substances did not absorb the amount of iodine which theory would require, *still, all the glycerides and fatty acids that occur in commercial* analysis of oils, fats, and waxes *do* conform with the theory. As the writer has found in his own experience, extending over many years, the iodine value may be relied upon as one of the safest guides in the technical analysis of fats.

The apparently capricious results which were obtained by different observers were explained by some chemists by the assumption that, simultaneously with the addition of iodine, or iodine chloride, substitution takes place in the molecule of the glycerides, with formation of hydriodic acid—much in the same way as substitution takes place in the case of bromine, with formation of hydrobromic acid (see above). But it has been shown by *Wijs*[5] that the free acid which was found in *Hübl's* solution after absorption had taken place was not hydriodic acid, but hydrochloric acid.

True, *Waller* previous to *Wijs* proved the occurrence of hydrochloric acid, but he erroneously ascribed its formation to a secondary reaction viz., the action of free chlorine on the water present. In this connection it may be pointed out that *Waller* proposed to render *Hübl's* solution more stable by the addition of hydrochloric acid to the iodine solution. A number of iodine determinations published by continental observers have been carried out by means of *Waller's* solution. This is prepared by dissolving 25 grms. of iodine in 200 c.c. of strong alcohol on the one hand, and 25 grms. of mercury bichloride in 200 c.c. of strong alcohol on the other, and then adding 25 grms. of strong hydrochloric acid, specific gravity 1·19, to the latter solution, finally mixing the two solutions, and making up to 500 c.c. with alcohol. It will be noticed that *Waller's* solution does not conform to *Hübl's* directions, namely, that there should be at least one molecule of mercury bichloride—27·5 grms.—to one molecule of iodine—25·4 grms. It will be further noticed that this solution is about twice as strong as the *Hübl* iodine solution.

[1] *Journ. prakt. Chem.* 1888 (37) 59.
[2] *Journ. f. prakt. Chemie*, 1894 (50) 75.
[3] *Ibid.* 1894 (50) 79.
[4] *Ibid.* 1894 (49) 61.
[5] *Zeit. f. analyt. Chem.* 1898, 277

Although the numbers obtained by *Waller's* method do not deviate widely from the *Hübl* numbers, the method is not free from objection, and will therefore not be considered in this work.[1]

The next important step in the explanation of the *Hübl* reaction was made by *Ephraim*.[2] He observed that the *Hübl* solution required a much larger amount of sodium thiosulphate after addition of potassium iodide than without it, and concluded therefrom that on mixing the components of the *Hübl* solution there is formed *at once* a substance capable of liberating iodine from potassium iodide.

The chemical change taking place in the iodine solution was expressed by *Ephraim* by the following equation:[3]—

$$HgCl_2 + I_2 = HgClI + ICl.$$

This equation would correspond to *Hübl's* directions, that for 2 atoms of iodine at least 1 molecule of mercury bichloride must be used. A solution of iodine monochloride of the same strength as the *Hübl* solution must contain 16·25 grms. in 1000 c.c. A number of experiments carried out with iodine monochloride solution of the specified strength on oleic acid, linseed oil, poppy seed oil, sesamé oil, almond oil, arachis oil, olive oil, and castor oil in the same fashion as in *Hübl's* iodine test, furnished results identical with those obtained by *Hübl's* method. *Ephraim* concludes, therefore, that alcoholic *solutions of iodine monochloride may be substituted for the Hübl* solution.

A confirmation of *Ephraim's* views, and of *Waller's* statement regarding the occurrence of hydrochloric acid is found in *Wijs*'[4] observations. These have led to a satisfactory explanation of the reactions occurring in the *Hübl* solution. The first change taking place on mixing the solutions of iodine and of mercury bichloride is represented by the following equation :—

$$HgCl_2 + 2I_2 = HgI_2 + 2ICl \quad . \quad . \quad . \quad . \quad (1).$$

It must be left an open question whether the action takes place in two stages, as shown by the two equations :—

$$HgCl_2 + I_2 = HgClI + ICl,$$
$$HgClI + I_2 = HgI_2 + ICl,$$

or not.

The equation (1) must be looked upon as representing a state of equilibrium between the four substances, since by dissolving mercury biiodide (HgI_2) in iodine chloride (ICl) solution, a mixture identical with the *Hübl* iodine solution is obtained. Equation (1) should therefore rather be considered a reversible equation, though the colour of the solution would point to a preponderance of the system

[1] Cp. also Ingle, *Journ. Soc. Chem. Ind.* 1902, 587.
[2] *Analyst*, 1895, 176.
[3] Ephraim states distinctly that this equation must not necessarily be considered as quantitatively expressing the chemical change.
[4] *Journ. Soc. Chem. Ind.* 1898, 698, *Zeit. f. ang. Chem.* 1898, 291.

$HgCl_2 + 2I_2$. Concurrently with this chief reaction, the following changes occur:—The ICl reacts with the water contained in the 95 per cent alcohol in the following manner:—

$$ICl + H_2O = HCl + HIO \quad . \quad . \quad . \quad . \quad . \quad (2),$$

but this change soon reaches a limit, since the HCl thus formed precludes the complete decomposition of the water present. The hypoiodous acid (IOH) is converted into iodic acid and free iodine, thus:—

$$5IOH = IO_3H + 2H_2O + 4I \quad . \quad . \quad . \quad . \quad . \quad (3),$$

although very slowly, for the amount of IOH is, as shown, a limited one. Since, however, the iodic acid will interact with free iodine and the hydrochloric acid in the solution to form ICl, as expressed by the equation:—

$$IO_3H + 4I + 5HCl = 5ICl + 3H_2O \quad . \quad . \quad . \quad . \quad (4),$$

it will be easily seen that a complicated system of equilibrium will result, the chief components of which are represented by the equation (2). Thus, we can assume in the *Hübl* iodine solution the presence of the following substances:—

$HgCl_2$, HgI_2, I, ICl, HCl, IOH, and IO_3H.

On standardising the iodine solution there is added potassium iodide solution and water. The changes taking place are expressed by the following equations:—

$$ICl + KI = KCl + I_2 \quad . \quad . \quad . \quad . \quad . \quad (5),$$

$$HCl + IOH + KI = KCl + H_2O + I_2 \quad . \quad . \quad . \quad (6),$$

$$IO_3H + 5HCl + 5KI = 5KCl + 3H_2O + 3I_2 \quad . \quad . \quad (7).$$

It will thus be seen that, provided no other reaction has taken place, the total amount of iodine originally employed when preparing the iodine solution must be found in the blank test as iodine, and further, that the final solution cannot contain free acid, provided the alcohol used was neutral.

Experiments, however, show (see p. 241) that the *Hübl* iodine solution loses strength rapidly at first, afterwards more slowly, and that the solution turns acid, the amount of acid corresponding exactly to the amount of iodine which has become inactive (has "disappeared"), except in the case of very old solutions, which are then found to contain acetic acid. The explanation of these phenomena is given by *Wijs* (in contradistinction to earlier explanations, assuming interaction between iodine and alcohol, with formation of hydriodic acid) as follows:—*A portion of the hypoiodous acid oxidises the alcohol to* aldehyde, as shown in the equation:—

$$2IOH + C_2H_6O = I_2 + H_2O + C_2H_4O \quad . \quad . \quad . \quad (8).$$

The equilibrium of the solution thus having been disturbed, fresh hypoiodous acid must be formed, but owing to the increased amount of hydrochloric acid now present, not quite the full quantity of

hypoiodous acid can be formed, notwithstanding that the free iodine, *liberated according to the last equation, interacts with* $HgCl_2$ (which is present in excess) to form fresh ICl, and consequently fresh IOH and HCl.

The oxidation of the alcohol, *the cause of the loss in strength of the iodine solution*, therefore proceeds much more slowly after a time, or, in other words, the older the solution the more stable it becomes. The acidity of the solution is, of course, explained by the excess of HCl which does not find sufficient IOH to be neutralised according to equation (6). The presence of aldehyde has been proved experimentally,[1] and since aldehyde is readily oxidised by the oxygen of the air to acetic acid, the excess of free acid in very old solutions is now easily explained by the slow oxidation of the aldehyde.

From the foregoing it would follow that by limiting the amount of hypoiodous acid that can be formed, say by excluding water, the *Hübl* solution must become more stable, and this logical postulate is borne out in practice when iodine solutions are prepared with absolute alcohol or ethyl acetate.

Again, if the decomposition of ICl, as explained by equation (2), is limited by disturbing the equilibrium through increasing the amount of hydrochloric acid at the outset, the same object must be reached. In fact this is the theoretical explanation for the greater stability of the *Waller* solution (see above), since sulphuric acid does not produce the same effect, and since the colour of the *Hübl* solution is rendered much lighter by the addition of hydrochloric acid, thus showing that the reaction represented by equation (2) has been much retarded.

Now, *Wijs* assumed that the active substance in the *Hübl* iodine solution is hypoiodous acid and not iodine monochloride. In support of his view, he quotes the following three arguments. (1) If iodine monochloride were the active substance, the halogen should be absorbed more rapidly from *Waller's* solution than from *Hübl's*, since ICl is present in greater concentration in the former solution than in the latter. But the reverse actually holds good, and this may be explained by the gradual or retarded formation of hypoiodous acid. (2) When a solution of hypoiodous acid (prepared by shaking an alcoholic iodine solution with freshly precipitated HgO and filtering off) is mixed with an oil, values identical with *Hübl* iodine numbers are obtained, the absorption being complete after ten seconds (one experiment only is given). (3) On increasing the concentration of IOH through addition of iodine, mercury bichloride, and water (which favour the formation of hypoiodous acid) more rapid absorption takes place, whereas it is retarded by those agents which reduce the IOH concentration, *e.g.* mercury bichloride and hydrochloric acid.

If *Wijs'* assumption were correct, there should be formed for each molecule of IOH absorbed by an oil one molecule of HCl, but although *some* acid is found, by no means the full quantity is obtained, and

[1] On shaking an alcoholic solution of iodine with HgO, aldehyde is formed.

thus *Wijs* is driven to the further, somewhat forced assumption that, taking oleic acid as an example, the reaction proceeds as follows :—

$$C_{18}H_{34}O_2 + HIO = C_{18}H_{34}O_2I.OH,$$
$$C_{18}H_{34}O_2I.OH + HCl = C_{18}H_{34}O_2ICl + H_2O.$$

It is evident that the final product is the same as is obtained by assuming that ICl is the active substance, and that ICl is absorbed as such. In fact, *Wijs'* proposal to substitute for *Hübl's* solution a solution of iodine monochloride in acetic acid (inasmuch as the preparation and the keeping of a solution of hypoiodous acid would offer almost insuperable difficulties), amounts practically to a tacit acceptance of the view that iodine chloride is the active agent.

The foregoing explanations show that *Hübl* has hit off in a happy and very ingenious manner the conditions most favourable for the obtainment of such values as are in close agreement with theory. It is therefore possible, if a sample contain the glyceride of *one* unsaturated fatty acid of known composition in admixture with glycerides of saturated fatty acids, to calculate the absolute amount of the glyceride of that unsaturated fatty acid. In cases of this kind the following table may be found useful. It will also guide the analyst as to the direction which further research should take in the case of samples of unknown composition, when of course the proportion of glycerides of unsaturated fatty acids cannot be calculated from the iodine value alone.

[TABLE

Acid.	Formula.	Iodine Value[1] of Fatty Acids.	Iodine Value of		
			Monoglyceride.	Diglyceride.	Triglyceride.
Tiglic	$C_5H_8O_2$	254·00	145·98	198·43	225·44
	$C_{12}H_{22}O_2$	128·28	93·38	112·39	120·57
	$C_{14}H_{26}O_2$	112·39	84·67	100·00	106·42
Hypogæic, Physetoleic, Lycopodic	$C_{16}H_{30}O_2$	100·00	77·44	90·07	95·25
Asellic	$C_{17}H_{32}O_2$	94·78	74·27	85·81	90·50
Oleic, Elaïdic, Isooleic, Rapic	$C_{18}H_{34}O_2$	90·07	71·35	81·93	86·20
Doeglic, Jecoleic	$C_{19}H_{36}O_2$	85·81	68·65	78·39	82·29
Erucic, Brassidic, Isoerucic	$C_{22}H_{42}O_2$	75·15	61·65	69·40	72·43
Linolic, Tariric, Millet oil, Telfairic, Elæomargaric	$C_{18}H_{32}O_2$	181·42	143·50	164·93	173·58
Linolenic, Isolinolenic, Jecoric	$C_{18}H_{30}O_2$	274·10	216·47	249·02	262·15
Isanic	$C_{14}H_{20}O_2$	461·82	345·57	409·67	436·67
Therapic	$C_{17}H_{26}O_2$	387·78	302·38	350·34	369·90
Ricinoleic, Isoricinoleic, Ricinelaidic, Ricinic	$C_{18}H_{34}O_3$	85·23	68·28	77·91	81·76
Mixed Triglycerides—					
Myristopalmitoolein	...	...	...	...	31·59
Oleodipalmitin	...	...	...	...	30·53
Oleodimargarin	...	...	...	...	29·53
Oleopalmitostearin	...	...	...	...	29·53
Oleodistearin	...	...	...	...	28·60
Elaïdodistearin	...	...	...	...	28·60

Ingle[2] recently instituted an inquiry into the origin and nature of the free acid which is formed in *Hübl's* reaction. He showed that the free acid is neither due to substitution (which has been proved before) nor to the splitting off of hydrochloric acid from the chloro-iodo-addition product, but that the formation of the free acids is caused by the action of water on the chloro-iodo-compound, and that the quantity of the acid thus formed depends on the chemical structure of the unsaturated compound, and also on the amount of water present.

Wijs' Modification of Hübl's Process

Wijs' iodine solution is prepared by dissolving separately 9·4 grms. (the correct figure being 9·3573) of iodine trichloride, and

[1] The atomic weight of iodine has been taken as 127.

[2] *Journ. Soc. Chem. Ind.* 1902, 587.

7·2 grms. (the correct figure being 7·1374) of iodine on the water-bath in glacial acetic acid, taking care that the solutions are protected from absorbing moisture whilst the dissolution takes place. The two solutions are then poured into a 1000 c.c. flask, and the flask filled up to the mark with glacial acetic acid. A cheaper way of preparing the solution (which commends itself in a laboratory where a large number of iodine tests are made) is to dissolve 13 grms. of iodine in a litre of glacial acetic acid, determining accurately the amount of iodine in it, and to pass washed and dried chlorine gas through it, until the titer of the original iodine solution is doubled. A little experience will readily show when this point is reached, as a very distinct change of colour takes place when all the iodine is converted into iodine monochloride. The glacial acetic acid must be pure, and should be tested by heating with potassium bichromate and concentrated sulphuric acid; even after prolonged standing a green tinge must not be noticeable.

The chloroform used in *Hübl's* process is preferably replaced by carbon tetrachloride, since commercial chloroform frequently contains some alcohol. The carbon tetrachloride must also be tested with potassium bichromate and concentrated sulphuric acid, for any admixture of oxidisable products.

In all other respects, including the excess of iodine chloride, the test is carried out in exactly the same manner as the *Hübl* iodine test, with this important difference, however, that it is not necessary to allow the solution to stand as prolonged a time as in the case of *Hübl's* test. In fact, in the case of oils and fats having an iodine value below 100, half an hour is quite sufficient for the completion of the reaction. Semi-drying oils require from half an hour to one hour, drying oils one hour, or at most two hours.

Wijs' solution possesses the further great advantage over *Hübl's* solution in that it keeps its titer unchanged for a considerable length of time. In fact, I can testify from my own experience that solutions kept for five months did not appreciably change the titer. Hence, for rapid work a blank test is not required in each case, and the determination of the iodine value can be carried out almost as rapidly as the determination of the saponification value.

Wijs[1] has shown that also with his solution, in the case of pure fatty acids, numbers are obtained which agree completely with theory, as is evidenced by the following table:—

Acid.	Experiment.	Theory.
Erucic acid	74·9	75·15
Brassidic acid	75·0	75·15
Elaïdic acid	90·0	90·07
Undecylenic acid	133·1	136·6
Oleic acid, commercial	87·6	90·07

[1] *Chem. Revue*, 1899, 1.

Furthermore, I[1] have shown that the iodine numbers obtained with *Wijs'* solution agree perfectly with those obtained by *Hübl's* method, provided the latter is carried out with all the precautions detailed above.

I can therefore thoroughly recommend *Wijs'* solution. It will be found preferable to the *Hübl* iodine solution, as it is infinitely superior to the latter as regards stability. Furthermore, it can be prepared rapidly, and the time spent on the test is very much shortened.

In addition to the original papers quoted already, the reader may be referred to those mentioned in the footnote.[2] *Hanus*,[3] following up a suggestion made by *Bellier*[4] recommends the substitution of iodine bromide by iodine chloride. Even if the same results be obtained as by *Wijs'* method (which is contested by *Marshall*[2] and also by *Harvey*[2]), it would appear to be a superfluous addition to a well-tried process.

As has been repeatedly stated, the subdivisions of the large classes of vegetable and animal oils, fats, and waxes adopted in this work are based on the magnitude of the iodine values. The following table enumerates most known oils, fats, and waxes. The subdivisions are arranged according to the magnitude of the iodine values, subject, however, to the grouping together of the members of some naturally related oils and fats, such as the rape oils, or the oils obtained from the fruits of the plants belonging to the *Rosifloræ*.

The numbers given are mean values, collated from the best observations. The individual observations are given under the heading of each oil, fat, or wax in Chapter XIV. In some cases I have thought it preferable to give the most reliable values instead of the mean values.

It will be seen that the oils, fats, and waxes arrange themselves in a natural order, from oils or fats of the highest iodine value, through small gradations to oils, fats, and waxes having the lowest iodine absorption.

[1] Lewkowitsch, *Analyst*, 1899, 259.

[2] A. H. Gill and W. O. Adams, *Journ. Amer. Chem. Soc.* 1900, 12. Lewkowitsch, *Analyst*, 1900, 33; *Jahrbuch der Chemie*, 1898, 395, 1902, 366. Wijs, *Analyst*, 1900, 33; *Zeits. f. Unters. d. Nahrgs. u. Genussm.* 1902, 497. A. Marshall, *Journ. Soc. Chem. Ind.* 1900, 213. F. W. Hunt, *Journ. Soc. Chem. Ind.* 1902, 454. T. F. Harvey, *Journ. Soc. Chem. Ind.* 1902, 1437. Tolman and Munson, *Journ. Amer. Chem. Soc.* 1903, 244.

[3] *Zeits. f. Unters. d. Nahrgs. u. Genussm.* 1901, 913. Cp. also C. A. Jungclaussen, *Chem. Centr.* 1901, ii. 1324; L. M. Tolman and L. S. Munson, *Journ. Amer. Chem. Soc.* 1902 (25), 244.

[4] *Annal. chim. analyt. appl.* 1900 (5), 128.

[TABLE

Iodine Values of Oils, Fats, and Waxes

Oil.	Class.	Group.	Iodine Value.
Perilla	Drying oils		206·1
Linseed			173-201
Tung oil			150-165
Lallemantia			162·1
Candle nut			163·7
Stillingia			160·6
White acacia			161·0
Cedar nut			159·2
Garden rocket			155·1
Hemp seed			148
Walnut, nut			145
Safflower			129·8-149·9
Echinops			138·1-141·2
Poppy seed			133-143
Henbane			138
Asparagus seed			138
Amoora			134·9
Niger seed			126·6-133·8
Sunflower			119-135
Yellow acacia			128·9
Para rubber tree seed			128·3
Celosia			126·3
Argemone			119·9-122·5
Fir seed			119·5
Madia			118·5
Indian laurel			118·6
Cameline	Semi-drying oils	Cotton seed oil group	135-142
Clover, red; white			124·3-119·7
Soja bean			121·7
Daphne oil			126·1
Pumpkin seed			123-130
Water melon			118
Maize (corn)			111-130
Wheat			115·4
Beech nut			104-111
Datura			113
Basswood			111·0
Kapok			116
Cotton seed			108-110
Sesamé			103-108
,, first expression			106-114
Lemon pips			109·2
Luffa seed			108·51
Brazil nut			106·2
Croton			102-104
Curcas, purging nut			98-110
Sorghum			98·9
Coumon			96·5
Pinot			136 (?)
Garden cress		Rape oil group	109
Ravison			101-122

Iodine Values of Oils, Fats, and Waxes—continued

Oil.	Class.	Group.	Iodine Value.
Hedge mustard	Semi-drying oils	Rape oil group	105
Rape (colza)			94-102
Black mustard			96-110
White mustard			92-97
Radish seed			93-96
Jamba			95·4
Small fennel	Non-drying oils		116·2
Quince			113·0
Cherry kernel			110-114
Cherry laurel			108·9
Apricot kernel			96-108
Plum kernel			93·3-100·3
Peach kernel			93-109
Almond			93-97
Wheat meal			101·5
Sanguinella			100·8
Acorn			100·7
Californian nutmeg			94·7
Arachis			83-100
Rice			96·4
Tea seed			88
Hazel nut			83-90
Pistachio			87·3
Koëme			86·2
Elderberry			81·41
Birch seed			83·6
Loue-Moue seed			87·0
Olive			79-88
Olive kernel			87·4
Coffee berry			85-87
Ungnadia			82·0
Ben			82
Strophantus			73·02
Tropaeolum			73·7
Paradise nut			71·64
Secale			71·0
Grape seed		Castor oil group	96
Castor seed			83-86
Menhaden	Marine animal oils	Fish oils	139-173
Sardine			161-193
Japanese sardine			100-164
Salmon			161·42
Herring			123·5-142
Stickleback			162·0
Sturgeon			125·3
Cramp fish			107·3
Sunfish			102·7
Cod liver		Liver oils	154·5-181·3 167
Haddock liver			154·2

Iodine Values of Oils, Fats, and Waxes—continued

Oil.	Class.	Group.	Iodine Value.
Skate liver	Marine animal oils	Liver oils	157·3
Tunny fish			155·9
Shark liver			114·6
Coal fish liver			137-162
Ling liver			132·6
Seal		Blubber oils	127-141
Whale			121-136
Turtle			112
Dugong			66·6
Dolphin body			99·5
Dolphin jaw			32·8
Porpoise jaw			22-50
Sheep's foot	Terrestrial animal oils		74·2
Horses' foot			73·8-90
Neat's foot			69·3-70·4
Egg			68·5-81·6
Pongam	Vegetable fats		89·4-90·4
Chaulmoogra			90·7
Laurel			68-80
Carapa			65-72·1
Margosa			69·6
Kodam seed			66-68·9
Mahua butter			53-67
Mowrah seed			50-62
Champaca			60-25
Shea butter			56·6
Palm oil			51·5
Akee oil			49·1
Macassar			48-55
Sawarri			49·5
Mafura tallow			45·5
Nutmeg butter			40-52
" "			(50-81)
Phulwara			42·1
Mkanyi			41·9
Rambutan tallow			39·4
Malabar tallow			38·2
Cacao butter			32-41
Vegetable tallow			19-38·3
Kokum butter			33·6
Borneo tallow			31 (?)
Dika oil			31·1
Muriti fat		Cocoa nut oil group	25·2
Mocaya oil			24·63
Cohune			13·2
Maripa			9·5
Palm nut oil			13-14
Cocoa nut oil			8-9·5
Cocos acrocomoides			4·8

Iodine Values of Oils, Fats, and Waxes—continued

Fat.	Class.	Group.	Iodine Value.
Tang kallak	Vegetable fats		11·5
Ucuhuba			9·5
Japan wax			4·9-8·5
Myrtle wax			2·9
Icebear	Animal fats	Drying fats	147
Blackcock			121·1
Hare			102·2
Rabbit (wild)			99·8
Rabbit (tame)		Non-drying fats	67·6
Wild duck			84·6
Domestic duck			58·5
Starling			83·7
Pigeon			82·3
Turkey			81·2
Fox			79·7
Horse			71-86
Horse marrow			79·1
Badger			71·3
Pine marten			70·2
Goose (domestic)			67-71
Goose (wild)			99·6
Chicken			66·7
Polecat			62·8
Human, adult			58·9-73·3
Lard			50-70
Fat from wild boar			76·6
Dog			58·5
Wild cat			57·8
Domestic cat			54·5
Beef marrow			55·4
Bone			45-55·8
Beef tallow			38-46
Mutton tallow			*35-46*
Butter			26-38
Elk			35·0
Reindeer			31·4-35·8
Roebuck			32·1
Fallow buck			26·4
Chamois			25·0
Stag			20·5-25·7
Sperm oil	Liquid waxes		81-90
Arctic sperm oil			67-82·1
Carnaüba wax	Solid waxes	Vegetable waxes	13·5
Flax wax			9·6
Wool wax		Animal waxes	17·1-28·9
Beeswax			7·9-11
Spermaceti			3·8
Insect wax			1·4

The determination of the iodine value furnishes one of the most valuable characteristics in technical fat analysis. If it be required to identify an oil, fat, or wax, the iodine value indicates in an unmistakable way the class to which it belongs. The iodine value will thus, as a rule, lead in the quickest possible manner to the identification of a given oil, fat, or wax. And, if a hitherto unknown specimen be under examination, the iodine value will at once point to the class or group in which the new oil or fat should be placed in the system.

This characteristic is all the more valuable as the age of an oil does not materially affect the iodine absorption provided the oil has not undergone any important change, such as oxidation. Changes due to oxidation are prominently noticeable in the case of drying, fish, and liver oils; less so in the case of the semi-drying and blubber oils. The influence of exposure to light and air on the iodine values of some oils has been examined systematically by *Ballantyne*.[1] His results are recorded in the following table:—

Kind of Oil.	Original Iodine Value.	After Six Months' Exposure to Sunlight.	
		Protected against Access of Air.	Exposed to Air.
Linseed oil . .	173·46	172·88	166·17
Cotton seed oil .	106·84	106·40	100·12
Rape oil . . .	105·59	105·27	102·13
Arachis oil . .	98·67	97·60	93·20
Castor oil. . .	83·63	83·27 (after 2 months)	83·27
Olive oil . . .	83·16	82·64	78·24

3. The Reichert (or Reichert-Meissl) Value

The Reichert (or Reichert-Meissl) value indicates the number of cubic centimetres of decinormal potash requisite for the neutralisation of that portion of the insoluble volatile fatty acids which is obtained from 2·5 (or 5) grms. of a fat or wax by the Reichert distillation process.

From the table containing the saponification values of pure triglycerides (p. 230), it will be gathered that the lower the molecular weight of the triglycerides, the higher is the saponification value of the glyceride. Hence, oils and fats containing notable quantities of glycerides of lower (volatile) fatty acids will be characterised by their saponification values exceeding 200.

There is no convenient method in use to determine quantitatively the amount of volatile fatty acids in a fat. *Reichert*[2] was the first to suggest a process (in the examination of butter) for estimating a definite proportion thereof. Although his process does not yield

[1] *Journ. Soc. Chem. Ind.* 1891, 31. [2] *Zeits. f. analyt. Chemie*, 18, 68.

absolute numbers, still it constitutes a valuable method as furnishing a measure of the total volatile acids. For purposes of comparison, especially so in the examination of butter fat, the relative numbers obtained thereby are of great importance in fat analysis.

Reichert originally proposed to ascertain the number of c.c. of decinormal alkali required for the saturation of the volatile fatty acids obtained from 2·5 grms. of an oil or fat, but at present it is customary to take 5 grms. of substance, as suggested by *Meissl*. In order to avoid errors, the quantity of fat to which the value relates should always be stated. In the following pages the *Reichert* (R.) value always refers to 2·5 grms. of fat, and the *Reichert-Meissl* (R.M.) *value* to 5 grms. of fat.[1]

The *Reichert* value being an arbitrary one, it is absolutely essential to adhere strictly to the conditions of operating described below.

Reichert's Process with *Meissl's Modification*.—Weigh off accurately 5 grms.[2] of the melted and purified fat in a flask of about 200 c.c. capacity, and add to it about 2 grms. of stick potash (conveniently kept in stock in pieces of about the same length) and 50 c.c. of 70 per cent alcohol. Saponify by heating on the water-bath with frequent shaking, until the alcohol has evaporated off completely. Dissolve the remaining soap paste in 100 c.c. of water, add 40 c.c. of dilute sulphuric acid (1 : 10) and a few small pieces of pumice. Fit to the flask a T-piece provided with a bulb, and connect with a *Liebig* condenser. Distil the liquid carefully so that 110 c.c. pass over within about one hour. They are received in a measuring flask, and 100 c.c. are filtered into another measuring flask. Add to the filtered liquid phenolphthalein, and titrate with decinormal caustic potash until the acid is exactly neutralised. The number of c.c. used is multiplied by 1·1 and thus the *Reichert-Meissl* value is obtained. (This value is about equal to the *Reichert* value multiplied by 2·2.)

Thus, if for 5 grms. of butter fat 28 c.c. of decinormal caustic alkali were required, the *Reichert-Meissl* value of that butter fat is 28.

It is hardly required to emphasise the necessity of using alcohol free from acid and aldehyde. The safest plan will be to work a blank test side by side with the sample, and to take the difference found as the actual result. Even with the purest alcohol a slight acidity will be noticeable in the blank test. Impure alcohol gives rise to the formation of acetic acid and should therefore be rejected altogether.

It should be distinctly understood that by this distillation process a portion only of the volatile fatty acids is recovered. *Richard Meyer* has shown that on distilling in a current of steam a value greater by 25 per cent is obtained. (Cp. also chap. viii. p. 343.) Hence the necessity of always working under strictly the same conditions.

[1] It should be noted that the Reichert-Meissl value is not necessarily twice the Reichert value.

[2] *Dingl. Polyt. Journ.* 233, 229.

Along with the volatile acids traces of higher fatty acids will pass over; they will be found in the distillate as minute oily drops or solid particles; but they do not vitiate the result, as they are removed by the subsequent filtration. (Cp. "Butter Fat," chap. xiv.)

The excellent *Reichert* process has not escaped the fate of nearly all modern methods used in fat analysis, viz. to receive at the hands of numerous analysts a number of supposed improvements, most of which are altogether insignificant or at best offer doubtful advantage.

Wollny[1] has raised a number of objections to the foregoing process, pointing out the following sources of error:—(1) absorption of carbon dioxide during saponification, introducing an error up to 10 per cent; (2) formation of esters during the saponification, causing a loss of 8 per cent; (3) formation of esters during the distillation with a loss of 5 per cent; (4) coherence of the fatty acids during the distillation, which may, in some cases, involve a loss of as much as 30 per cent; (5) the form and size of the distillation flask and the time the distillation lasts, which may influence the result to the extent of ± 5 per cent.

These objections have been refuted by *v. Raumer* and *Sendtner*. However, a number of determinations, carried out by various chemists according to *Wollny's* somewhat too detailed modifications, have found a place in the literature of the subject. But since the process has been adopted by a joint committee of the Government Laboratory and the Society of Public Analysts as the standard method for the determination of volatile fatty acids in margarine and butter, I describe it as published by the committee.[2]

Reichert-Wollny Modification.—Five grams of liquefied fat are introduced into a 300 c.c. flask, of the form seen in the figure (length of neck 7 to 8 centimetres, width of neck 2 centimetres). Two c.c. of a caustic soda solution, prepared by dissolving 98 per cent sodium hydrate in an equal weight of water—protected from the action of atmospheric carbonic acid—and 10 c.c. of alcohol (of about 92 per cent) are added, and the mixture is heated under a reflux condenser, connected with the flask by a T-piece, for fifteen minutes in a bath containing boiling water. The alcohol is evaporated off by heating the flask on the water-bath for about half an hour, or until the soap is dry. One hundred c.c. of hot water which have been kept boiling for at least ten minutes are added, and the flask heated until the soap is dissolved. Forty c.c. of normal sulphuric acid and three or four fragments of pumice or broken pipe-stems are added, and the flask is at once connected with a condenser by means of a glass tube 7 millimetres wide, and 15 centimetres from the top of the cork to the bend. At a distance of 5 centimetres above the cork is a bulb 5 centimetres in diameter. The flask is supported on a circular piece of asbestos 12 centimetres in diameter, having a hole in the centre 5 centimetres in diameter, and is first heated by a very small flame, to fuse the insoluble fatty

[1] *Journ. Soc. Chem. Ind.* 1887, 831. [2] *Analyst*, 1900, 309.

acids, but the heat must not be sufficient to cause the liquid to boil. The heat is increased, and when fusion is complete 110 c.c. are distilled off into a graduated flask, the distillation lasting about 30 minutes (say from 28 to 32 minutes); the distillate is shaken, 100 c.c. are filtered off, transferred to a beaker, 0·5 c.c. of phenolphthalein solution (1 grm. in 100 c.c. alcohol) added, and the filtrate titrated with decinormal soda or baryta solution. In precisely the same manner (with the same reagents), a blank test should be made, and the amount of decinormal alkali required to neutralise the distillate ascertained. This should not exceed 0·3 c.c. The volume of decinormal solution of alkali used, less the figure obtained by the

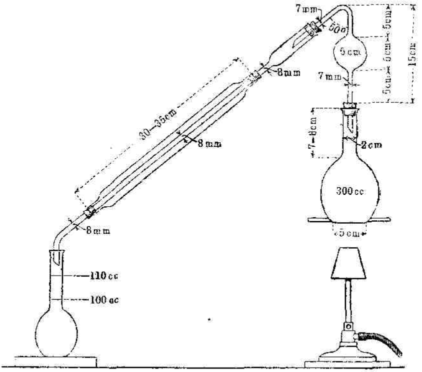


Fig. 35.

blank experiment, is multiplied by 1·1. The number so found is the *Reichert-Wollny* number.

The well-known fact that in the *Reichert* distillation process only part of the volatile acids is distilled off,[1] has induced some analysts to modify it and to attempt to obtain the total quantity. Thus it has been proposed to repeat the distillation several times with fresh quantities of water. But not only does this take up more time than can be conveniently allowed for a technical analysis, but a source of error is thereby introduced, inasmuch as with each distillation decomposition of the non-volatile acids takes place.

[1] *H. D. Richmond* states (*Analyst*, 1895, 218) that by the *Reichert-Wollny* process, in the case of butters, only about 87 per cent of the total volatile acids is found in the distillate. I found for 2·5 grms. of butter fat by distilling 500 c.c. the number of c.c. decinormal potash required = 22. (Cp. also chap. viii. p. 343.)

In order to obviate the formation of ethylic esters of the volatile fatty acids (*Wollny's* second objection), *Leffmann* and *Bean*[1] (cp. chap. xiv.) propose to saponify with a concentrated solution of caustic soda in glycerol.

Instead of saponifying the fat with alkali, *Kreiss* proposed, especially in the case of butter fat, to saponify with concentrated sulphuric acid. *This method cannot be recommended.* The details of the method and a criticism thereof will be given later on under the heading "Butter Fat" (chap. xiv.).

Since the volatile fatty acids of butter fat are for the most part also soluble in water, several methods have been proposed having for their object the determination of the *soluble* acids.

These methods consist in saponifying the sample exactly in the manner described under the heading "saponification value." Thus, the amount of potassium hydrate required to neutralise the fatty acids is determined first. The soap solution is then decomposed with mineral acid and the liberated fatty acids washed on a filter with hot water (see p. 263) until the soluble fatty acids have been removed.

The insoluble acids are then dissolved in alcohol and titrated with standardised potash. By subtracting the amount of caustic potash thus found from the quantity used for saponification, the amount of caustic potash required for the neutralisation of the soluble (volatile) fatty acids is obtained.

It is evident that by adopting a method of this kind, the determination of the neutralisation values of the insoluble fatty acids and the soluble fatty acids can be carried out with one and the same quantity. The values thus obtained in the case of butter fat nearly coincide with those obtained by *Reichert's* distillation process, but are by no means identical with them. For this reason, these methods cannot be recommended to replace the *Reichert* distillation process. In the case of the fats belonging to the cocoa nut oil group the errors may be much greater. (Cp. "Butter Fat," chap. xiv.)

Most of the naturally occurring oils and fats contain but small quantities of volatile (soluble) fatty acids. Therefore, the *Reichert* values of the majority of oils, fats, and waxes are very low. As a rule they are below 0·5; hence, the *Reichert-Meissl* values of the majority of oils, fats, and waxes are below 1·0. It is evident, therefore, that a somewhat high *Reichert-Meissl* value will be a distinctive characteristic of a fat or wax, and that very valuable indications as to the nature of a fat or wax will be obtained by the determination of the volatile acids by the *Reichert-Meissl* process.

In the following table I collate those oils, fats, and waxes which can be distinguished from all others by their *Reichert-Meissl* numbers:—

[1] *Analyst*, 1891, 153; cp. also Karsch, *Chem. Ztg.* 1896, 207.

Reichert (R.) and Reichert-Meissl (R.M.) Values

Yellow acacia oil	2·7 (R.M.)
Clover, red ; white	3·3 ; 3·5 (R.M.)
Maize (corn) oil	4·2-9·9 (R.)
Croton oil	12-13·6 (R.M.)
Small fennel oil	5·4 (R.M.)
Wheatmeal oil	2·8 (R.M.)
Turtle	4·6 (R.M.)
Dugong	2·5 (R.)
Dolphin oil	5·6 (R.)
Dolphin jaw oil	65·92 (R.)
Porpoise body oil	23·5 (R.)
Porpoise jaw oil	47·77-65·8 (R.)
Carapa fat	2·2 (?) (R.M.)
Macassar oil	9 (R.M.)
Nutmeg butter	1-4·2 (R.M.)
Muriti fat	5·0 (R.M.)
Mocaya oil	7·0 (R.M.)
Maripa oil	4·45 (R.M.)
Palm nut oil	5-6 (R.M)
Cocoa nut oil	7-8·4 (R.M.)
Butter fat	27-29 (R.M.)
Flax wax	9·27 (R.M.) (?)

The extraordinarily high numbers of porpoise and dolphin oils are due to the presence of the glyceride of valeric acid. Amongst the solid fats, butter fat is notable on account of its high *Reichert-Meissl* value. Therefore, this number affords a most valuable means of identifying butter fat, and readily distinguishing it from other fats.

4. The Hehner Value

The Hehner value indicates the sum of insoluble fatty acids and unsaponifiable matter in a fat or wax, expressed in per cents.

This number may be determined by one of the following methods :—

(*a*) *Hehner's Method.*[1]—Weigh accurately some filtered fat contained in a small beaker furnished with a glass rod, and pour about 3-4 grms. (the exact quantity being determined by re-weighing) into a porcelain dish of about 5 inches diameter. Add 50 c.c. of strong alcohol and 1-2 grms. of solid caustic potash, and heat on the water-bath with constant stirring until a clear solution is obtained. After about five minutes, allow one drop of distilled water to fall into the solution. If the saponification is complete the solution will remain clear ; if, however, a turbidity is noticed, the heating must be continued until this test indicates that all the fat has been saponified. Then boil down the clear solution of soap to pastiness, dissolve in 100 to 150 c.c. of

[1] *Zeitsch. f. analyt. Chemie*, 1877, 145.

water, and acidify with dilute sulphuric acid. Next heat the liquid until the liberated fatty acids float on the top as a clear oily layer. Filter through a paper of about 4·5 inches diameter, previously dried at 100° C. and accurately weighed in a small beaker (covered with a watch-glass). The filter-paper should be of stout material, ordinary filtering paper readily allowing the liquid to run through turbid. A good plan is to have the filter half full of hot water before any fatty matter is transferred to it, keeping it full till all the liquid is added. Finally, wash the fatty acids on the filter with boiling water until a few c.c. of the wash-water does not redden sensitive tincture of litmus. For 3 grms. of fat sometimes 2000 to 3000 c.c. of wash-water are required in order to completely remove the last traces of the acids occupying an intermediate place between soluble and insoluble acids (as lauric acid). The washing being completed, immerse the funnel with the filter in a vessel of cold water, so that the water outside and the acids inside are at the same level. Allow the water then to drain off, transfer the filter to the beaker in which the filter has been weighed, and dry at 100° C. for two hours. Weigh accurately, dry for another hour or hour and a half, and weigh again. The difference between the two weights will, as a rule, be below 1 milligrm. Completely concordant results cannot be expected, the two chief sources of error, however, tending to compensate each other—one causing an increase, the other a decrease in weight. For on the one hand any unsaturated acids may become oxidised, whilst on the other hand loss is incurred through slight volatilisation of fatty acids.

The following table, due to *Tatlock*,[1] will give some indications as to the amount of error caused by drying fatty acids at 90° C.:—

[1] *Journ. Soc. Chem. Ind.* 1890, 374.

[TABLE

Table showing Loss (or Gain) in Weight of Dry Fatty Acids, during different Periods, at 90° C.

Time heated at 90° C.	Fatty Acids from								Stearic Acid.	Olive Oil containing 9·42 per cent Free Oleic Acid.	Olive Oil from which Free Fatty Acid was removed.
	Olive Oil (1).	Olive Oil (2).	Olive Oil (3).	Olive Oil (4).	Castor Oil.	Rape Oil.	Cotton Seed Oil.	Linseed Oil.			
Dry.	100·00.	100·00.	100·00.	100·00.	100·00.	100·00.	100·00.	100·00.	100·00.	100·00.	100·00.
24 hours	99·22	99·33	99·18	99·50	99·18	100·50	99·26	101·25	100·08	100·24	100·88
48 ,,	98·88	98·92	98·85	99·06	98·51	100·30	99·04	101·23	100·06	100·52	101·42
72 ,,	...	...	...	98·70	97·85	99·89	...	...	99·72	100·52	101·32
96 ,,	98·18	98·20	98·17	...	...	...	98·12	100·42	...	...	
120 ,,	...	...	...	98·09	96·82	99·46	97·87	100·19	98·22	100·10	100·36
192 ,,	96·96	97·08	96·97								
360 ,,	95·45	95·50	95·42								
528 ,,	94·14	94·17	94·10								
720 ,,	92·62	92·67	92·57								

(*b*) *Dalican's Method*.[1]—Melt 10 grms. of fat in a flask of 250 to 300 c.c. capacity, and saponify with 80 c.c. of 85 per cent alcohol and a solution of 6 grms. of caustic soda in 6 to 8 c.c. of water on the water-bath. The saponification will, as a rule, be complete after thirty to forty minutes. Leave the flask on the water-bath until all the alcohol has evaporated off, dissolve the soap in 150 c.c. of water, and add gradually, in small quantities, 25 c.c. of hydrochloric acid (1 volume of concentrated acid diluted with 4 volumes of water), agitating the contents of the flask after each addition of acid. Heat the flask for another thirty minutes on the water-bath, until the fatty acids have separated on the top as a transparent oily layer; then remove the flask from the bath and cool thoroughly. After about two hours break the cake of fatty acids with a glass rod, and pour off the liquid through a plain filter. Then melt the fatty acids over 100 c.c. of boiling water and add 150 c.c. more boiling water. Allow to stand forty minutes, cool thoroughly, and proceed as before. Repeat this process of washing until litmus paper dipped in the wash-water does not turn red after twenty minutes' standing. As a rule, eight to ten washings will be found sufficient for the complete removal of the soluble fatty acids. Next transfer the insoluble fatty acids to a porcelain dish, and wash the flask thoroughly with boiling water, passing all the wash-waters through the filter, which must be kept moist, so as to allow the small quantity of fatty acids adhering to it to be easily united with the bulk. Finally heat the dish from 100° to 110° C. for one hour at first, and then, after weighing, again for twenty minutes until the weight remains fairly constant.

(*c*) *Knight's Process*.[2]—*J. West Knight* rejects *Hehner's* process on account of the difficulty of avoiding loss during the various operations, and proposes a method based on the insolubility of the barium salts of the higher fatty acids in water on the one hand, and on the ready solubility of the barium salts of the volatile acids on the other.

The following is a description of *Knight's* process:—1-3 grms. of the dried and filtered fat are saponified by heating on the water-bath with twice their volume of alcoholic potash for about half an hour. The solution is then brought up to 300 c.c. with cold distilled water, and an aqueous solution of barium chloride is added until no further precipitation takes place. The precipitate is collected on a filter, washed with warm water, and then transferred to a Muter tube. Next the barium salts are decomposed with hydrochloric acid, and the liberated fatty acids shaken up with ether, in which they dissolve easily. The ethereal solution is made up to 100 c.c., and an accurately measured quantity—say 50 c.c.—is run off into a weighed flask. The ether is then distilled off and the dried residue weighed.

Inasmuch as the solubility of the acids may not correspond to the solubility of their barium salts, it is open to doubt whether the results obtained by the last method will agree with those found by the methods described above. However, the numbers published by

[1] *Moniteur scient.* 12, 989. [2] *Analyst*, 1881, 155.

Knight agree closely with those obtained by *Hehner's* method. Hence, *Knight's* process must be considered a correct one, although the use of an ethereal solution and the measuring off of an aliquot part is likely to introduce errors.[1]

As pointed out above, the *Hehner* value represents the *total* insoluble fatty matter obtained on saponifying a fat or wax. Only in the case of pure triglycerides is the *Hehner* value identical with the percentage of insoluble fatty acids.

Since the theoretical yields of the insoluble fatty acids from their monoglycerides, diglycerides, and triglycerides are useful as a guide in the examination of oils and fats, I have calculated the theoretical numbers and collated them in the following table :—

Percentages of Insoluble Fatty Acids in Mono-, Di-, and Triglycerides

Glyceride of Acid.	Monoglyceride.	Diglyceride.	Triglyceride.
Acetic	0	0	0
Butyric	0	0	0
Valeric	0	0	0
Caproic	0	0	0
Caprylic	–	–	–
Capric	–	–	–
Lauric	–	–	–
Myristic	75·50	89·05	94·75
Palmitic	77·58	90·15	95·29
Daturic	78·49	90·60	95·52
Stearic	79·33	91·02	95·73
Oleic	79·22	90·95	95·70
Linolic	79·10	90·90	95·67
Linolenic	78·98	90·83	95·63
Ricinoleic	80·12	91·43	95·93
Arachidic	80·82	91·76	96·09
Erucic	82·04	92·35	96·39
Cerotic	84·26	93·40	96·90
Melissic	85·93	96·17	92·27
Hydroxystearic	80·2	91·47	95·95
Dihydroxystearic	81·02	91·87	96·15
Trihydroxystearic	81·78	92·23	96·35
Sativic	82·48	92·56	96·50
Linusic	83·70	93·15	96·77
Mixed Triglycerides—			
Myristopalmitoolein	...	...	95·3
Oleodipalmitin	...	...	95·3
Stearodipalmitin	...	...	95·44
Oleodimargarin	...	...	95·58
Oleopalmitostearin	...	...	95·58
Palmitodistearin	...	...	95·59
Daturodistearin	...	...	95·66
Oleodistearin	...	...	95·62
Elaidodistearin	...	...	95·62

[1] Asbóth states that also the lead salts of the volatile acids are soluble in water. But as his paper does not furnish any proof for this assertion, his statement must be accepted with reserve.

In the case of the easily soluble fatty acids I have placed a zero, and in the case of the intermediate fatty acids which are only soluble in large quantities of water I have placed a – in the respective columns.

On glancing at the numbers given in the last column it will be seen that the differences between the values for palmitin, stearin, olein, linolin, linolenin, and ricinolein are so small that they fall within the errors of the gravimetric method. Hence, in these cases the discriminative value of the *Hehner* number would appear to be *nil*. It only then acquires importance when a mixture of the glycerides named with glycerides of fatty acids below myristic acid is under examination. In that case the *Hehner* value will be below 95, and from the difference between the number found and 95 a measure is obtained of the amount of glycerides of lower fatty acids in a natural product. The *Hehner* value therefore indicates in a direct manner what can be gathered from a saponification value exceeding 200, or from a *Reichert-Meissl* value exceeding 5 (cp. table, *Reichert - Meissl* value). Indeed, the determination of the *Hehner* value had been proposed in the first instance for the examination of butter fat, in which the percentage of insoluble fatty acids falls below 90 per cent.

The *Hehner* values of the majority of oils and fats lie in the neighbourhood of 95. The following table contains a list of those oils and fats which largely deviate from this number :—

Oil or Fat.	Hehner Value.
Maize (corn)	88·2-95·7
Croton	89·0
Small fennel	88·8
Elderberry	91·75
Shark liver	86·9 (?)
Dolphin jaw oil	66·28
Porpoise jaw oil	70·23
Carapa	93·7
Macassar	91·5
Maripa	88·88
Palm nut oil	87·6-91·1
Cocoa nut oil	88·6-90
Japan wax	90·6
Butter	86·5-89·8

It will be seen that with the exception of Japan wax the oils and fats here enumerated occur in the table of *Reichert* and *Reichert-Meissl* values. In the case of Japan wax the occurrence of a dibasic acid explains the low *Hehner* number.

Since all natural glycerides contain small proportions of unsaponifiable matter, which is insoluble in water, it will be isolated together with the insoluble fatty acids. Therefore, in the case of the natural oils and fats, the *Hehner* value is greater than the proportion of insoluble fatty acids. In the majority of cases the

amount of unsaponifiable matter is so small that for practical purposes it may be neglected. Hence, the *Hehner* value of oils and fats is frequently considered as identical with the amount of insoluble fatty acids. In the case of maize oil, which contains a somewhat high amount of unsaponifiable matter, this procedure is not admissible.

This inadmissibility becomes important in the case of waxes. As the fatty matter obtained on saponifying the waxes and decomposing the soap by means of mineral acid contains both the fatty acids and the alcohols (which are insoluble in water), the *Hehner* value thus found will even exceed 100, water having been assimilated during the saponification, and this value would then be misleading; therefore it is not customary to determine the *Hehner* value in the case of waxes, other characteristics more readily enabling us to distinguish them from glycerides.

In case it be desired to determine the amount of insoluble fatty acids in waxes, the fatty matter obtained on saponification must be freed from the alcohols first (cp. p. 294). The following table contains the proportions of insoluble fatty acids in some waxes as ascertained in my laboratory.

Wax.	Percentage of Fatty Acids.
Sperm oil	60-64
Arctic sperm oil	61-65
Carnaüba wax	47·95
Wool wax	59·8
Beeswax	46·77
Spermaceti	53·45
Insect wax	51·54

The Acetyl Value

The acetyl value indicates the number of milligrams of caustic potash (KOH) required for the neutralisation of the acetic acid obtained on saponifying one gram of the acetylated fat or wax.

The determination of the acetyl value (acetyl number) of oils and fats is based on the principle that glycerides containing hydroxylated fatty acids assimilate, on heating with acetic anhydride, one or more acetyl groups, according as the fatty acids contain one or more alcoholic hydroxyl groups. The chemical change consists in the replacing of the hydrogen atom of the alcoholic hydroxyl group or groups by the radicle of acetic acid, as explained by the following equations:—

$$\underset{\text{Ricinolein.}}{C_3H_5[O.C_{18}H_{32}O(OH)]_3} + \underset{\text{Acetic anhydride.}}{3(C_2H_3O)_2O} = \underset{\text{Acetyl ricinolein.}}{C_3H_5[O.C_{18}H_{32}O(O.C_2H_3O)]_3} + \underset{\text{Acetic acid.}}{3C_2H_4O_2}.$$

$$\underset{\text{Sativin.}}{C_3H_5[O.C_{18}H_{31}O.(OH)_4]_3} + \underset{\text{Acetic anhydride.}}{6(C_2H_3O)_2O} = \underset{\text{Tetra-acetyl sativin.}}{C_3H_5[O.C_{18}H_{31}O.(O.C_2H_3O)_4]_3} + \underset{\text{Acetic acid.}}{6H_2O}.$$

The determination of the acetyl value (first proposed by *Benedikt*, see below) is carried out in the form given it by *Lewkowitsch*:[1]—10

[1] *Journ. Soc. Chem. Ind.* 1897, 503.

grms., or any other convenient number of grams, are boiled with twice the amount of acetic anhydride for two hours in a round-bottomed flask attached to an inverted condenser. The solution is then transferred to a beaker of about 1 litre capacity, mixed with 500 to 600 c.c. of boiling water and heated for half an hour, whilst a slow current of carbon dioxide is passed into the liquid through a finely-drawn-out tube reaching nearly to the bottom of the beaker; this is done to prevent bumping. The mixture is then allowed to separate into two layers, the water is syphoned off, and the oily layer again boiled out in the same manner three successive times. The last trace of acetic acid is thus removed, as may be ascertained by testing with litmus paper. Prolonged washing beyond a certain limit causes slight dissociation of the acetyl product. This would lead to too low an acetyl value. The acetylated product is then filtered through a dry filter-paper in a drying oven to remove water.

The whole operation may be carried out quantitatively, and in that case the fatty matter is treated in a fashion similar to the *modus operandi* described for the determination of the *Hehner value* (p. 262). It may be useful to work quantitatively if it is desired to ascertain preliminarily whether a notable amount of glycerides of hydroxy acids be present in an unknown fat (cp. chap. vi. p. 289).

About 5 grms. of the acetylated product are then saponified by boiling with alcoholic potash, as in the determination of the saponification value. If the "distillation process" be adopted, it is not necessary to work with an accurately measured quantity of standardised alcoholic potash. In case the "filtration process" be used, the alcoholic potash must be measured exactly. (It is advisable to use in either case a known volume of standard alkali, as one is then enabled to determine the saponification value of the acetylated oil or fat.) Next the alcohol is evaporated off and the soap dissolved in water. From this stage the determination is carried out either by (*a*) the distillation process, or (*b*) filtration process.

(*a*) *Distillation Process.*—Add dilute sulphuric acid (1:10), more than is required to saturate the potash used, and distil the liquid in a current of steam. 600-700 c.c. of water are distilled off. As a rule this will be quite sufficient, and the last 100 c.c. will be found to require no more than 0·1 c.c. of decinormal alkali. Then titrate the distillate with decinormal potash, using phenolphthalein as an indicator, multiply the number of c.c. by 5·61, and divide by the weight of substance taken. This gives the acetyl value.

(*b*) *Filtration Process.*—Add to the soap solution a quantity of standardised sulphuric acid *exactly* corresponding to the amount of alcoholic potash employed and warm gently, whereupon the fatty acids will readily collect on the top as an oily layer. (If the saponification value has been determined, it is of course necessary to take into account the volume of acid used for titrating back the excess of potash.) Filter off the liberated acids, wash with boiling water until the washings are no longer acid, and titrate the filtrate with decinormal alkali. The acetyl value is calculated in the manner shown above (*a*).

Both methods give identical results; the latter requires less time and will therefore be found more convenient.

The distilled water used in determining the value by either the distillation or filtration process should be carefully freed from carbonic acid by previous boiling, as otherwise serious errors may result. Even the water used for generating steam in the distillation process should be brought into violent ebullition before the steam is passed into the distilling flask. This source of error may easily creep in in the case of very hard water. Check experiments with pure acetic acid will readily guide the operator. In order to facilitate the separation of the insoluble fatty acids in the filtration process, it will be found useful to add a slight excess of mineral acid. Of course this amount must be measured accurately and deducted from the alkali required for determining the dissolved acids.

Pure triglycerides containing no hydroxylated acids have no acetyl value; pure glycerides of hydroxylated fatty acids yield acetyl numbers in complete agreement with theory. In these cases the acetyl value is a *constant*. The following table contains the theoretical acetyl numbers of some triglycerides:—

Glyceride.	Formula.	Molecular Weight.	Saponification Value.	Insoluble Fatty Acids.	Acetyl Value.
			Mgrms. KOH.	Per cent.	Mgrms. KOH.
Ricinolein . .	$C_3H_5[O . C_{18}H_{32}O(O . C_2H_3O)]_3$	1058	318·2	84·49	159·1
Hydroxystearin .	$C_3H_5[O . C_{18}H_{34}O(O . C_2H_3O)]_3$	1064	316·3	84·56	158·1
Dihydroxystearin	$C_3H_5[O . C_{18}H_{33}O(O . C_2H_3O)_2]_3$	1238	407·8	76·67	271·9
Trihydroxystearin	$C_3H_5[O . C_{18}H_{32}O(O . C_2H_3O)_3]_3$	1412	476·8	70·54	357·6
Sativin . .	$C_3H_5[O . C_{18}H_{31}O(O . C_2H_3O)_4]_3$	1586	530·5	65·81	424·3
Linusin . .	$C_3H_5[O . C_{18}H_{29}O(O . C_2H_3O)_6]_3$	1934	609·2	58·94	522·1

In practical analysis, if a mixture of a pure glyceride of hydroxylated acids of known composition with a pure glyceride which is free from hydroxylated acids be given, the determination of the acetyl value enables us to calculate the proportion of the glyceride of the former.

A case of this kind is exemplified by castor oil, which consists to a very large extent of ricinolein. The foregoing table gives the acetyl value of pure ricinolein as 159·1. Suppose the determination of a commercial sample of castor oil gave the acetyl value 150·3; then the percentage of ricinolein in the sample will be found from the proportion 159·1 : 100 : : 150·3 : x; x = 94·4 per cent.

Free alcohols undergo the same change on heating with acetic anhydride, that is, they also assimilate an acetyl group in exchange for the hydrogen atom in the alcoholic hydroxyl group. This is exemplified by the following equations:—

$$\underset{\text{Cetyl alcohol.}}{C_{16}H_{33}OH} + \underset{\text{Acetic anhydride.}}{(C_2H_3O)_2O} = \underset{\text{Cetyl acetate.}}{C_{16}H_{33}O . C_2H_3O} + \underset{\text{Acetic acid.}}{C_2H_4O_2}.$$

$$\underset{\text{Glycerol.}}{C_3H_5(OH)_3} + \underset{\text{Acetic anhydride.}}{3(C_2H_3O)_2O} = \underset{\text{Triacetin.}}{C_3H_5(O . C_2H_3O)_3} + \underset{\text{Acetic acid.}}{3C_2H_4O_2}.$$

The following table gives the theoretical acetyl values of a number of pure alcohols :—

Acetate of	Formula.	Molecular Weight.	Acetyl Value.
Cetyl alcohol	$C_{16}H_{33}O \cdot C_2H_3O$	284	197·5
Octodecyl alcohol	$C_{18}H_{37}O \cdot C_2H_3O$	312	179·8
Ceryl alcohol	$C_{26}H_{53}O \cdot C_2H_3O$	424	132·3
Myricyl alcohol	$C_{30}H_{61}O \cdot C_2H_3O$	480	116·9
Cholesterol / Phytosterol	$C_{26}H_{43}O \cdot C_2H_3O$	414	135·5
Glycerol	$C_3H_5O_3(C_2H_3O)_3$	218	772·0

From the acetyl value the proportion of pure alcohols can be calculated, provided their composition be known. Thus the proportion of glycerol in a commercial glycerin can be determined by its acetyl value (cp. **Glycerol**, p. 286).

If the chemical composition of a hydroxylated triglyceride contained in an oil or fat, or of an alcohol contained in a wax, be unknown, then the acetyl value would still be a measure of the hydroxylated triglycerides or of the alcohols respectively. If both hydroxylated triglycerides and alcohols be present simultaneously, the acetyl value would naturally be a measure of the sum of both, viz., hydroxylated triglycerides and alcohols. Even in the latter somewhat more complicated case, the acetyl value would still rank as a constant, just like the saponification value or the *Reichert-Meissl* value does.

The foregoing remarks apply to pure triglycerides and waxes, and hold good as long as no other substances capable of assimilating acetyl groups be present. It has, however, been pointed out already that natural oils and fats contain varying quantities of free fatty acids (see below, **Acid Value**), due to the varying amount of hydrolysis the natural oils and fats had undergone. These partially hydrolysed natural oils and fats contain some mono- and diglycerides which are capable of assimilating acetyl groups by exchanging the hydrogen of their alcoholic hydroxyl group or groups for an acetyl group or groups, as exemplified by the following two equations :—

$$\underset{\text{Monostearin.}}{C_3H_5(OH)_2(O \cdot C_{18}H_{35}O)} + (C_2H_3O)_2O = \underset{\text{Di-acetyl-monostearin.}}{C_3H_5(O \cdot C_2H_3O)_2(O \cdot C_{18}H_{35}O)} + H_2O.$$

$$\underset{\text{Distearin.}}{C_3H_5(OH)(O \cdot C_{18}H_{35}O)_2} + (C_2H_3O)_2O = \underset{\text{Acetyl distearin.}}{C_3H_5(O \cdot C_2H_3O)(O \cdot C_{18}H_{35}O)_2} + C_2H_4O_2.$$

This will be readily seen from the following table, stating the acetyl values of pure mono- and diglycerides. In the case of those mono- and diglycerides which contain hydroxylated fatty acids in the molecule, an additional amount of acetic anhydride will be assimilated, thus increasing the acetyl value of such glycerides considerably.

Acetyl Values of Pure Mono- and Diglycerides

Glyceride of Acid.	Acetylated Monoglyceride.			Acetylated Diglyceride.		
	Formula.	Molecular Weight.	Acetyl Value.	Formula.	Molecular Weight.	Acetyl Value.
1. Acetic	$C_3H_5(O.C_2H_3O)_2(O.C_2H_3O)$	218	772·0	$C_3H_5(O.C_2H_3O)(O.C_2H_3O)_2$	218	772·0
2. Butyric	$C_3H_5(O.C_2H_3O)_2(O.C_4H_7O)$	246	684·2	$C_3H_5(O.C_2H_3O)(O.C_4H_7O)_2$	274	614·3
3. Valeric	$C_3H_5(O.C_2H_3O)_2(O.C_5H_9O)$	260	647·4	$C_3H_5(O.C_2H_3O)(O.C_5H_9O)_2$	302	557·3
4. Caproic	$C_3H_5(O.C_2H_3O)_2(O.C_6H_{11}O)$	274	614·3	$C_3H_5(O.C_2H_3O)(O.C_6H_{11}O)_2$	330	510·0
5. Caprylic	$C_3H_5(O.C_2H_3O)_2(O.C_8H_{15}O)$	302	557·3	$C_3H_5(O.C_2H_3O)(O.C_8H_{15}O)_2$	386	436·0
6. Capric	$C_3H_5(O.C_2H_3O)_2(O.C_{10}H_{19}O)$	330	510·0	$C_3H_5(O.C_2H_3O)(O.C_{10}H_{19}O)_2$	442	380·8
7. Lauric	$C_3H_5(O.C_2H_3O)_2(O.C_{12}H_{23}O)$	358	470·1	$C_3H_5(O.C_2H_3O)(O.C_{12}H_{23}O)_2$	498	338·0
8. Myristic	$C_3H_5(O.C_2H_3O)_2(O.C_{14}H_{27}O)$	386	290·7	$C_3H_5(O.C_2H_3O)(O.C_{14}H_{27}O)_2$	554	101·3
9. Palmitic	$C_3H_5(O.C_2H_3O)_2(O.C_{16}H_{31}O)$	414	271·0	$C_3H_5(O.C_2H_3O)(O.C_{16}H_{31}O)_2$	610	91·99
10. Daturic	$C_3H_5(O.C_2H_3O)_2(O.C_{17}H_{33}O)$	428	262·1	$C_3H_5(O.C_2H_3O)[O.C_{17}H_{33}O]_2$	638	87·9
11. Stearic	$C_3H_5(O.C_2H_3O)_2(O.C_{18}H_{35}O)$	442	253·9	$C_3H_5(O.C_2H_3O)(O.C_{18}H_{35}O)_2$	666	84·24
12. Oleic	$C_3H_5(O.C_2H_3O)_2(O.C_{18}H_{33}O)$	440	255·0	$C_3H_5(O.C_2H_3O)(O.C_{18}H_{33}O)_2$	662	84·74
13. Linolic	$C_3H_5(O.C_2H_3O)_2(O.C_{18}H_{31}O)$	438	256·2	$C_3H_5(O.C_2H_3O)(O.C_{18}H_{31}O)_2$	658	85·28
14. Linolenic	$C_3H_5(O.C_2H_3O)_2(O.C_{18}H_{29}O)$	436	257·3	$C_3H_5(O.C_2H_3O)(O.C_{18}H_{29}O)_2$	654	85·78
15. Arachidic	$C_3H_5(O.C_2H_3O)_2(O.C_{20}H_{39}O)$	470	238·7	$C_3H_5(O.C_2H_3O)[O.C_{20}H_{39}O]_2$	722	77·7
16. Erucic	$C_3H_5(O.C_2H_3O)_2(O.C_{22}H_{41}O)$	496	226·2	$C_3H_5(O.C_2H_3O)(O.C_{22}H_{41}O)_2$	774	72·5
17. Cerotic	$C_3H_5(O.C_2H_3O)_2(O.C_{26}H_{51}O)$	554	202·5	$C_3H_5(O.C_2H_3O)(O.C_{26}H_{51}O)_2$	890	63·05
18. Melissic	$C_3H_5(O.C_2H_3O)_2(O.C_{30}H_{59}O)$	610	183·9	$C_3H_5(O.C_2H_3O)[O.C_{30}H_{59}O]_2$	1002	55·9
19. Ricinoleic	$C_3H_5(O.C_2H_3O)_2[O.C_{18}H_{32}O(O.C_2H_3O)]$	498	338·0	$C_3H_5(O.C_2H_3O)[O.C_{18}H_{32}O(O.C_2H_3O)]_2$	778	216·3
20. Hydroxystearic	$C_3H_5(O.C_2H_3O)_2[O.C_{18}H_{34}O(O.C_2H_3O)]$	500	336·7	$C_3H_5(O.C_2H_3O)[O.C_{18}H_{34}O(O.C_2H_3O)]_2$	782	215·3
21. Dihydroxystearic	$C_3H_5(O.C_2H_3O)_2[O.C_{18}H_{33}O(O.C_2H_3O)_2]$	558	402·2	$C_3H_5(O.C_2H_3O)[O.C_{18}H_{33}O(O.C_2H_3O)_2]_2$	898	312·4
22. Trihydroxystearic	$C_3H_5(O.C_2H_3O)_2[O.C_{18}H_{32}O(O.C_2H_3O)_3]$	616	455·4	$C_3H_5(O.C_2H_3O)[O.C_{18}H_{32}O(O.C_2H_3O)_3]_2$	1014	387·4
23. Sativic	$C_3H_5(O.C_2H_3O)_2[O.C_{18}H_{31}O(O.C_2H_3O)_4]$	674	499·3	$C_3H_5(O.C_2H_3O)[O.C_{18}H_{31}O(O.C_2H_3O)_4]_2$	1130	446·8
24. Linusic	$C_3H_5(O.C_2H_3O)_2[O.C_{18}H_{29}O(O.C_2H_3O)_6]$	790	568·1	$C_3H_5(O.C_2H_3O)[O.C_{18}H_{29}O(O.C_2H_3O)_6]_2$	1362	535·5

The amount of hydrolysis the natural oils and fats undergo is a varying quantity, therefore the amount of monoglycerides and diglycerides will vary accordingly, and likewise the acetyl value will vary.

It follows, then, that in the case of the natural oils, fats, and waxes, with the exception of castor oil, the acetyl value will be a *variable*. It may be emphasised again that in the case of castor oil *the acetyl value is a constant, because castor oil is practically a pure* triglyceride of ricinoleic acid or of its isomerides.

In the determination of the acetyl value of the natural oils and fats which contain volatile or soluble fatty acids, this number would include the volatile fatty acids as well. Therefore, without a correction, the acetyl values found will be too high by the amount due to the volatile acids. I have therefore termed the acetyl values found direct "apparent acetyl values." The *true* acetyl value is found by determining the amount of potash required to saturate the volatile acids of the original oil or fat in precisely the same manner, and deducting the number thus obtained from the apparent acetyl value.[1] In the following table I give a list of a number of acetyl values determined by the above-described method, after deducting the *amount of potash required by the volatile acids naturally present*, from the apparent acetyl values. The acetyl values contained in the following table represent, therefore, the *true acetyl values*:—

Oil or Fat.	True Acetyl Value.
Linseed	3·98
Candle nut	9·86
Safflower	16·1
Rape oil	14·7
Arachis	9·06
Hazel nut	3·2
Olive	10·64
Elderberry	15·5
Japanese sardine	13·0
Cod liver	4·8
Skate liver	10·6
Shark liver	11·9
Seal	16·5
Horses' foot	*13·0*
Neat's foot	22·0
Palm	18
Sawarri	7·0
Cacao butter	2·8
Palm nut	1·9-8·4
Cocoa nut	0·9-12·3
Japan wax	27-31·2
Lard	2·6
Beef marrow	4·2
Bone	11·3
Beef tallow	2·7-8·6
Butter	1·9-8·6

[1] Cp. chap. viii. "Volatile Fatty Acids."

Oil or Wax.	True Acetyl Value.
Sperm	4·5-6·4
Arctic sperm	4·1-6·4
Carnaüba wax	55·24
Wool wax	23·3
Beeswax	15·24
Spermaceti	2·63

These true acetyl values must not be looked upon as constants, but as variables furnishing a measure of the amount of mono-, and diglycerides present in oils and fats, due to hydrolysis. They also include that amount of potash which is required for the saponification of the acetylated cholesterol or phytosterol.

I have further pointed out[1] that the acetyl value may be made to furnish a measure of the state of rancidity if considered in conjunction with the acid value (see below).

The acetyl value was first proposed by *Benedikt* as a constant in the examination of oils and fats, and the process given by *Benedikt* and *Ulzer*[2] for its determination applied to the *insoluble fatty acids*, and not to the oils and fats themselves. In this process the amount of alkali was determined which was required to neutralise 1 grm. of acetylated fatty acids—"acetyl acid value"—and further, in a second experiment, the amount of potash required both to saturate the free acid and to combine with the acetyl group split off on boiling with alcoholic potash—"acetyl saponification value." The difference of the two amounts of alcoholic potash was termed by *Benedikt* the "acetyl value."

The neutralisation and the saponification of the acetylated acids were therefore supposed to take place in two stages according to the following equations:—

1. $C_{17}H_{32}(O \, . \, C_2H_3O) \, . \, COOH + KOH = C_{17}H_{32}(O \, . \, C_2H_3O)COOK + H_2O.$
Acetyl-ricinoleic acid. Potassium salt.

2. $C_{17}H_{32}(O \, . \, C_2H_3O)COOK + KOH = C_{17}H_{32}(OH)COOK + C_2H_3O_2K.$
Potassium acetyl-ricinoleate. Potassium ricinoleate.

The hydroxyl in the carboxyl group of the fatty acids should therefore not have been affected by the acetic anhydride during the acetylating process. Fatty acids containing no alcoholic hydroxyl, such as stearic, oleic, etc., should not yield an acetyl value, the acid and saponification values in these cases being identical.

Lewkowitsch,[3] however, has shown that pure capric, lauric, palmitic, stearic, cerotic, and oleic acids gave very considerable acetyl values when treated according to *Benedikt* and *Ulzer's* process. This result could only be explained by the fact that the fatty acids had been con-

[1] Cp. Lewkowitsch, "The Meaning of the Acetyl Value in Fat Analysis," *Analyst*, 1899, 319.

[2] *Monatshefte für Chemie*, 8, 40; cp. Lewkowitsch, *Analysis of Oils, Fats, and Waxes*, 2nd edition, p. 163.

[3] *Proc. Chem. Soc.* 1890, 72, 91; *Journ. Soc. Chem. Ind.* 1890, 660.

verted into their anhydrides, the acetic anhydride acting in the manner explained by the following equation :—

$$2C_{15}H_{31}\,.\,COOH + \underset{\text{Acetic anhydride.}}{\begin{matrix}C_2H_3O\\C_2H_3O\end{matrix}\!\!>O} = \underset{\text{Palmitic anhydride.}}{\begin{matrix}C_{15}H_{31}CO\\C_{15}H_{31}CO\end{matrix}\!\!>O} + 2C_2H_3O\,.\,OH.$$

Palmitic acid. Acetic anhydride. Palmitic anhydride. Acetic acid.

The anhydrides were thus actually obtained, and their great stability in presence of even boiling water was proved.

When these anhydrides were dissolved in *cold alcohol* for the purpose of titrating, on adding the potash, hydrolysis of the anhydrides took place at once to a certain extent, and as the acid combined with a certain quantity of potash, an (apparent) acid value of the substance was obtained. When, however, the anhydrides were shaken up with *water*, the first drop of potash gave in the presence of phenolphthalein a pink colouration, which disappeared but slowly. Thus in the *alcoholic* solution a partial hydrolysis of the anhydrides took place, hydrolysis ceasing when an equilibrium was established in the solution. Under these conditions apparent acetyl values were obtained for the fatty acids above mentioned, these acetyl numbers being, in truth, fictitious values.

Hydroxylated fatty acids are certainly acetylated when boiled with acetic anhydride, but simultaneously the acetylated acids are converted into their anhydrides in consequence of the large excess of acetic anhydride used. During the subsequent boiling with water, a portion of the anhydrides may or may not become hydrolysed, thus yielding possibly a mixture of free acetylated acids and acetylated anhydrides.

When this mixture is dissolved in alcohol and titrated with caustic potash, after neutralisation of the free acids, if any, partial hydrolysis will set in, as explained above in the case of capric acid, etc., and an "acid value" will thus be obtained (*Benedikt's* "acetyl acid value"). But such "acid value" will be lower than the neutralisation value of the acetylated fatty acids, the anhydrides remaining unacted on to a certain extent. Consequently the saponification value of the acetylated product (*Benedikt's* "acetyl saponification value") will be found too high, since the not-hydrolysed anhydrides are saponified subsequently by the boiling alcoholic potash. The difference between saponification and "acid" values, supposed to be the acetyl value of the acids, will therefore be devoid of any quantitative meaning.

The same conclusion, of course, holds good in the case of a mixture of hydroxy and ordinary fatty acids.

The **true** acetyl value of the **fatty acids**, however, is found, according to *Lewkowitsch*,[1] by actually determining the amount of acetic acid assimilated by the hydroxy acids in the form of acetyl (C_2H_3O) and combining, on saponification, as acetic acid with alkali.

[1] *Journ. Soc. Chem. Ind.* 1890, 846.

This is done by boiling the acetylated product with alcoholic potash and estimating the acetic acid formed as described above.

It is therefore evident that the "acetyl values" found by various observers working according to *Benedikt* and *Ulzer's* method must be accepted with the greatest reserve.

Correct acetyl values of the fatty acids can only be obtained by the last-named method in the case of a *triglyceride* of hydroxylated fatty acids, provided also that the anhydrides formed are completely converted into fatty acids. In fact *Benedikt* and *Ulzer's* method had been worked out with castor oil, and the satisfactory result found in this case has led to a generalisation which must be considered inadmissible. Hence, most numbers contained in the literature of our subject pointing to the presence of hydroxylated fatty acids in natural oils and fats, with the exception of castor oil and perhaps grape seed oil, and those oils which do contain hydroxylated acids (quince oil), must be rejected as fictitious values.

In special cases the determination of the acetyl value of the *fatty acids* will lead to important information (see below), but for the reasons set out above, the acetyl value should be determined by *Lewkowitsch's* method. It should, however, be remembered that the acetyl value would then refer to the insoluble fatty acids and not to the oils and fats themselves. Thereby this important disadvantage is introduced, that all indications as to the presence of mono- and diglycerides are obliterated. Furthermore, important differences existing between the various glycerides present in oils and fats disappear at the outset, for in the process of preparing the fatty acids the soluble acids are washed away. This occurs notably in the case of blown oils (see chap. xv.). In such cases it is advisable to determine the acetyl value of the original oil or fat as well as that of its insoluble fatty acids. If both numbers are practically identical, the conclusion can be drawn that the acetyl value is owing to a triglyceride of hydroxylated fatty acids. This exactly happens in the case of castor oil.

To sum up, the acetyl value of an oil or fat will be a **constant** if *tri*glycerides only are present. Otherwise the acetyl value will be a **variable** indicating, in addition to hydroxylated fatty acids, the following substances:—alcohols, monoglycerides and diglycerides, oxidised acids (see chap. viii.), and "unknown acids" (see chap. viii.). The acetyl value may also be indicative of rancidity in an oil or fat.

If a **free alcohol** is acetylated, no complication through formation of anhydrides can arise, and in that case simply the saponification value of the acetylated product — the acetate of the alcohol —is determined. This value is also the acetyl value of the alcohol (the saponification value of the original alcohol being of course *nil*).

B. VARIABLES

1. The Acid Value

The acid value indicates the number of milligrams of potassium hydrate required to saturate the free fatty acids in one gram of a fat or wax; or, in other words, *it gives the amount of potassium hydrate, expressed in tenths per cent, necessary to neutralise the free fatty acids in one gram of a fat or wax.* This value is therefore a measure of the free fatty acids in a fat or wax.

For the determination of the acid value of a fat or wax the sample is dissolved in alcohol (purified methylated spirit), or in methyl alcohol or amyl alcohol,[1] or a mixture of alcohol and ether, and titrated with aqueous or alcoholic standard alkali, phenolphthalein being used as indicator.

The standard alkali may be, according to the quantity of fat available for the analysis, half-, or tenth-normal. Some analysts prefer an alcoholic standard solution to an aqueous one, although the accuracy of the analysis is *not* increased thereby. On the contrary, an alcoholic standard solution has the drawback of altering its titer more quickly, and therefore requiring occasional re-standardising. The end-point of titration is distinctly recognisable, saponification of the neutral fat not taking place immediately through the small excess of alkali necessary to produce the pink colouration. On standing, however, for some time, even if access of air and consequently decolouration due to absorption of carbonic acid be excluded, the pink colour will disappear in some cases, owing to saponification of neutral esters[2] taking place. This will be especially the case if the specimen under examination were dissolved in ether-alcohol. It would, obviously, be erroneous to add more alkali from time to time as the pink colouration disappears.

Mineral acid in the sample must, of course, be first removed by washing with water, and the solvents employed should be tested for acidity. Before using the solvent it will be best to neutralise it exactly with decinormal alkali, phenolphthalein being the indicator.

Liquid fats are weighed off or measured off accurately in a flask, neutralised alcohol and a few drops of phenolphthalein solution are then added, and the liquid is titrated with constant shaking. Convenient quantities are 10 grms. (or 10 c.c.) of oil and 50 c.c. of alcohol, to be titrated with standardised alkali.

Solid fats must be heated with the alcohol on the water-bath so that the fat is liquefied; they are then titrated in the same manner. Should the fat solidify during the operation, the flask must be heated again before the titration can be brought to an end. Of course, to guard

[1] Halphen, *Ann. chim. anal. appl.* 1901 (6), 133.
[2] Lewkowitsch, *Journ. Soc. Chem. Ind.* 1890, 846.

against partial saponification of the neutral fat, excess of alkali must be avoided. If it should be deemed preferable to work with clear solutions, the fat may be dissolved in a mixture consisting of two parts of ether and one part of alcohol, and then titrated with alcoholic standard solution. *Archbutt* proposes to use as solvent methyl alcohol (purified by distilling it twice).

One or two examples will illustrate the method of calculating the acid value.

1. Weighed off 3·254 grms. of tallow. Required for neutralising the free fatty acids 3·5 c.c. decinormal caustic potash (or soda) or 3·5 × 5·61 milligrms. KOH. The amount of KOH required for 1 grm. of tallow, or its acid value, is therefore

$$A = \frac{3{\cdot}5 \times 5{\cdot}61}{3{\cdot}254} = 6{\cdot}03.$$

2. Measured off 25 c.c. of olive oil, spec. grav. 0·917. Required for neutralising the free fatty acids 9·4 c.c. of a solution of caustic potash, 1 c.c. of which contains 0·0257 grms., or 25·7 milligrms. KOH. The weight of the oil is 25 × 0·917 = 22·925 grms., therefore

$$A = \frac{9{\cdot}4 \times 25{\cdot}7}{22{\cdot}925} = 10{\cdot}5.$$

The proportion of free fatty acids in an oil or fat is frequently expressed in a different manner.

In this country, especially in the case of oils, it is usual to calculate the free acid as oleic acid, molecular weight 282, and to express the amount of free fatty acids in per cents of the fat. Thus in the first example the percentage of free fatty acids would be returned as

$$\frac{3{\cdot}5 \times 0{\cdot}0282}{3{\cdot}254} \times 100 = 3{\cdot}03\ \%,$$

and in the second example

$$\frac{9{\cdot}4 \times 0{\cdot}0257 \times 0{\cdot}282}{0{\cdot}0561 \times 22{\cdot}925} \times 100 = 5{\cdot}28\ \%.$$

Since the molecular weight of oleic acid, 282, is approximately five times 56·1 (the molecular weight of KOH), and the acid value expresses the amount of KOH in tenths per cent, a rapid and in many cases sufficiently accurate method of converting the acid value into per cents of oleic acid is to multiply the former by 0·5.

In other cases, as for lubricating oils, the free fatty acids are sometimes expressed in terms of sulphuric anhydride, SO_3, and the result is given in per cents of the oil employed. Thus in the first example we would find

$$\frac{3{\cdot}5 \times 0{\cdot}004}{3{\cdot}254} \times 100 = 0{\cdot}43\ \%,$$

and in the second

$$\frac{9{\cdot}4 \times 0{\cdot}0257 \times 0{\cdot}04}{0{\cdot}0561 \times 22{\cdot}925} \times 100 = 0{\cdot}75\ \%.$$

Köttstorfer expresses the acidity by the number of c.c. of normal potash required for 100 grms. of the fat. In this connection the number of c.c. is termed "degrees of acidity."

In the subjoined table a comparison is made of the different methods of expressing the acidity; an easy calculation allows of transforming one term into any other.

Acid Value, being $\frac{1}{10}$ per cent of KOH.	Oleic Acid, Per cent.	Sulphuric Anhydride, Per cent.	Degrees Köttstorfer, being c.c. normal KOH per 100 grms. Fat.
1	0·5027	0·0713	1·782
1·9893	1	0·1418	3·546
14·0250	7·0500	1	25·000
0·5610	0·2820	0·0400	1

The acid value is not a constant, and the but too frequent references in the literature of our subject to this value as a constant are entirely misleading. The acid value of natural oils and fats is a **variable**, entirely depending on the state of purity of an oil, on its age, the amount of hydrolysis it has suffered, and the amount of oxidation it has undergone. In the case of fresh oils and fats, as has been pointed out already, the quantity of free fatty acid is so small that it may be considered negligible. Vegetable oils seem to contain small quantities of free fatty acids, whereas animal fats in a fresh state are practically devoid of free fatty acids. It has also been pointed out that if oils and fats are left in contact with putrescible or fermentable matter, the amount of free fatty acids may rapidly increase, rising to 70 and even to 100 per cent, as in the case of *old palm oil*. *The importance of the acid value consists* therefore in that it indicates the quality of an oil or fat. It shows the amount of hydrolysis an oil or fat has undergone, and in *conjunction with the acetyl value it may indicate the amount of* lower fatty acids that have been formed by destruction and the amount of hydroxylated acids formed subsequently, in the wake of *hydrolysis*.

In case the nature of the free acid, and consequently its molecular weight, be known, the absolute quantity of free acid may be calculated, as shown above for oleic acid. *In such cases the table* given below (p. 333) may be found useful.

Since the acid values are variables, no useful purpose would be served here by giving a list of the acid values of the natural oils and fats. The numbers found in practice for such specimens as were submitted to examination will be given under the heading of the individual oils and fats in Chapter XIV.

In the case of waxes, the acid values vary in a lesser degree than in the case of oils and fats, and a certain proportion of free fatty acids, varying within narrow limits, seems to be characteristic of carnaüba wax and beeswax (chap. i.).

It is evident that if an oil or fat consists exclusively of neutral triglycerides, its acid value will be *nil*. In that case the saponification value will indicate the amount of caustic potash required to saponify the *neutral esters*, or, in other words, the amount of potash required to neutralise the combined fatty acids. But if the oils and fats contain free fatty acids, that is, if they exhibit a definite acid value, then the saponification value will be the sum of the amounts of caustic potash requisite to neutralise the free fatty acids and those fatty acids which have been combined with glycerol as esters. The difference between these two amounts of potash has been termed hitherto the "ester value" (ether value). Thereby was understood the number of milligrams of potassium hydrate required for the saponification of the neutral esters in one gram of an oil or fat. Writers who termed the acid value a constant were naturally bound to look also on the ether value as a constant. As I have shown that the acid value is a variable, it is evident that the ether value must also be a variable. This is exemplified by the following table, part of which has been given above :—

Variations of Saponification and "Ester" Values

Stearin. Per cent.	Stearic Acid. Per cent.	Saponification Value.	Acid Value.	"Ester" Value.
100	0	189·1	0	189·1
75	25	191·02	49·37	141·65
50	50	193·30	98·75	94·55
25	75	195·41	148·13	47·28
0	100	197·5	197·5	0

But even with these restrictions, the ester value could only have a meaning in the absence of mono- and diglycerides. Since, however, the presence of free fatty acids points to previous hydrolysis of neutral triglycerides, and since this hydrolysis conditions the presence of mono- and diglycerides, the so-called ester value loses its meaning, inasmuch as that part of caustic potash which is required for the saponification of the esters refers to a mixture of triglycerides, diglycerides, and monoglycerides. Hence it follows that all the numerous references in the fat literature to ester values of oils and fats are more or less valueless.

Since in the solid waxes—carnaüba wax and beeswax—the acid value varies within circumscribed limits, the ester value likewise varies within definite limits, and hence a certain amount of importance has been attached to the ester value in the analysis of beeswax. But since even here the ester value is merely a number obtained by the difference of two numbers (namely, saponification value *minus* acid value), it is unnecessary to introduce a new number. Therefore I consider it advisable to omit, even in the case of waxes, any reference to an ester value.

2. Glycerol

According to the fundamental equation, in which R stands for the radicle of any fatty acid—

$$C_3H_5(OR)_3 + 3KOH = C_3H_8O_3 + 3KOR,$$

3 molecules of caustic potash are required for the saponification of 1 molecule of neutral fat, yielding 1 molecule of glycerol. Therefore, for every 168·3 grms. of KOH used, 92 grms. of glycerol will be obtained; consequently 1 grm. of KOH is equivalent to 0·54664 grms. of glycerol.

In the case of pure triglycerides, the proportion of glycerol is a constant (cp. following table), and the quantity of glycerol yielded by an oil or fat can be calculated from the saponification value as shown. In the case of natural oils and fats, a calculation of this kind would lead to erroneous results, not only on account of the small quantities of unsaponifiable matter that are always present, but chiefly on account of the proportion of free fatty acids and of lower glycerides, mono- and diglycerides, occurring in the natural oils and fats in variable quantities. Therefore the percentage number of glycerol must be looked upon as a variable.

The proportion of glycerol yielded by mono- and diglycerides is placed side by side with that yielded by triglycerides in the following table :—

[Table

Percentages of Glycerol obtained on saponifying Tri-, Di-, and Monoglycerides

Glyceride of Acid.	Triglyceride.	Diglyceride.	Monoglyceride.
Acetic	42·20	52·27	68·65
Butyric	30·46	39·66	56·80
Valeric	26·74	35·38	52·27
Caproic	23·96	31·94	48·42
Caprylic	19·58	26·74	42·20
Capric	16·67	23·00	37·40
Laurie	14·42	20·18	33·58
Myristic	12·74	17·97	30·46
Palmitic	11·42	16·20	27·88
Daturic	10·85	15·44	26·74
Stearic	10·34	14·74	25·70
Oleic	10·41	14·84	25·85
Linolic	10·48	14·93	25·99
Linolenic	10·55	15·03	26·14
Ricinoleic	9·87	14·11	24·74
Arachidic	9·45	13·52	25·83
Erucic	8·74	12·57	22·33
Cerotic	7·50	10·85	19·58
Melissic	6·60	9·79	17·49
Hydroxystearic	9·81	14·03	24·60
Dihydroxystearic	9·33	13·37	23·59
Trihydroxystearic	8·90	12·78	22·66
Sativic	8·51	12·24	21·80
Linusic	7·81	11·28	20·26
Mixed Triglycerides—			
Acetodiformin	48·4		
β-Acetodibutyrin	33·6		
Myristopalmitoolein	11·4		
Oleodipalmitin (Dipalmitoolein)	11·06		
Stearodipalmitin (Dipalmitostearin)	11·03		
Oleodimargarin (Oleodidaturin)	10·69		
Oleopalmitostearin (Stearopalmitoolein)	10·69		
Palmitodistearin (Distearopalmitin)	10·67		
Daturodistearin (Distearodaturin)	10·50		
Oleodistearin	10·4		
Elaidodistearin	10·4		

From the foregoing it will be readily seen that, *e.g.* rancid tallow may yield a larger quantity of glycerol than can be calculated from the mixture of tripalmitin, tristearin, and triolein.

For the determination of the proportion of glycerol which a fat yields on saponification, several methods have been proposed. (It would be incorrect to speak of the proportion of glycerol in a fat since glycerol is formed only on saponification.)

The older processes having for their object to isolate the glycerol

and weigh it, as in *Chevreul's* original method, are not suitable as quantitative methods. On the one hand they yield results below the truth, owing to volatilisation of small quantities of glycerol at 100° C. (p. 132). (This source of error is avoided in *David's* process,[1] in which the concentration of the glycerol solution is not carried so far that loss is incurred, but it introduces another error through the necessity of saponifying with barium hydrate (cp. p. 56).) On the other hand the product so obtained is always contaminated with foreign substances, and therefore too high results are obtained.

The determination of glycerol is, therefore, best carried out by indirect methods.

(1) *Determination of Glycerol by Oxidation Processes*

On oxidising glycerol in a strongly alkaline solution at the ordinary temperature with potassium permanganate, it is converted quantitatively into oxalic acid, carbon dioxide, and water, according to the following equation :—

$$C_3H_8O_3 + 3O_2 = C_2H_2O_4 + CO_2 + 3H_2O.$$

This reaction, originally suggested by *Wanklyn* and *Fox*,[2] has been worked out as a basis for a quantitative method by *Benedikt* and *Zsigmondy*[3] in the following manner :—Saponify 2 to 3 grms. of the sample of fat with caustic potash and pure methyl alcohol, evaporate off the latter, dissolve the soap in hot water, and decompose with dilute hydrochloric acid. Then warm until the liberated fatty acids have separated out as a clear oily layer. In the case of a liquid fat some paraffin wax is best added so as to obtain a solid cake on cooling. Next filter from the fatty acids into a spacious flask, wash well, and neutralise with caustic potash, using methylorange as an indicator. Then add 10 grms. of caustic potash in sticks, and run in a 5 per cent solution of potassium permanganate until the liquid no longer appears green, but blue or blackish. Instead of a solution, finely powdered potassium permanganate crystals may also be used. Next heat the liquid to the boiling point,[4] when hydrated manganese dioxide separates, and the solution becomes red ; discharge the colour by adding carefully the quantity of sulphurous acid solution required (but not more) for the reduction of the excess of the permanganate, taking care that the solution still remains strongly alkaline. Filter through a plain filter of sufficiently large size to hold at least one-half of the liquid, and well wash the precipitate with boiling water. It may happen that with the last wash-waters, small quantities of hydrated manganese dioxide pass through the filter, but this does not at all interfere with the accuracy of the process.

Acidify the filtrate with acetic acid, whereby sufficient sulphurous acid is set free to reduce the manganese dioxide, and heat the solu-

[1] *Compt. rend.* 94 (1882), 1477. [2] *Chem. News*, 53, 15.
[3] *Journ. Soc. Chem. Ind.* 1885, 610.
[4] It is not advisable to keep the solution at the boiling point for any length of time.

tion, which should be about 600 to 1000 c.c., almost to the boiling point, and precipitate with 10 c.c. of a 10 to 12 per cent solution of calcium chloride or calcium acetate. (If more of the precipitant be used, considerable quantities of calcium sulphate are thrown down, vitiating the quantitative determination.) The precipitate contains silicic acid in addition to calcium oxalate, hence the amount of oxalic acid cannot be calculated from the weight of the calcium carbonate (or calcium oxide) obtained on ignition. Therefore the amount of oxalic acid must be either determined volumetrically, or inferred from the alkalinity of the ignited residue. In the latter case dissolve the ignited precipitate in an accurately measured excess of half-normal hydrochloric acid, and titrate with half-normal caustic soda, using methylorange as an indicator. Eighty parts of sodium hydrate are equivalent to 92 parts of glycerol.

Allen[1] has somewhat modified this process and suggests the following *modus operandi* :—The fat is saponified with aqueous caustic potash in a closed flask. The oxidation is effected as described above, but sodium sulphite is used for reducing the excess of permanganate. The liquid containing the precipitated hydrated peroxide of manganese is then poured into a 500 c.c. flask, made up to 500 c.c., and 15 c.c. of hot water are added above the mark, this being an allowance for the volume of the precipitate and for the expansion of the hot liquid. The solution is next poured through a dry filter, and 400 c.c. of the filtrate, when cold, are measured off accurately, acidulated with acetic acid, and precipitated with calcium chloride. The precipitate is filtered off, washed well, and rinsed into a porcelain dish after piercing the filter. The neck of the funnel is then plugged and the filter filled with dilute sulphuric acid ; after standing for a few minutes it is allowed to run into the dish. Sufficient sulphuric acid is then added to bring the total amount of acid up to a quantity equal to 10 c.c. of concentrated sulphuric acid, when the solution is warmed to 60° C. and titrated with potassium permanganate. If decinormal permanganate be used, each c.c. used corresponds to 0·0045 grm. of $C_2H_2O_4$, or to 0·0046 grm. of glycerol.

With regard to this process the following notes will be found useful :—Methyl alcohol is used in the saponification of the fat instead of ethyl alcohol, as the latter may, under certain conditions of concentration, and for a definite percentage of alkali, give rise to the formation of oxalic acid. The errors resulting from this cause will be found to increase with the amount of alcohol retained by the soap on evaporation. On the other hand, if a complete elimination of the alcohol be attempted by repeated evaporation of the dissolved soap, loss of glycerol may result.

The liquid that is oxidised contains besides glycerol all the soluble fatty acids originally combined with it in the fat. On working strictly according to the directions given above, neither oxalic acid nor any other organic acid yielding a calcium salt insoluble in acetic acid will be formed. Therefore, it may be safely inferred that

1 *Commercial Organic Analysis*, ii. 290.

the presence of the soluble fatty acids does not interfere with the correctness of the determination of the glycerol. *Johnstone*,[1] it is true, maintains that in presence of butyric acid the process is useless, this acid being nearly all converted into oxalic acid, but both *Hehner*[2] and *Mangold*[3] have shown that in the process as given by *Benedikt* and *Zsigmondy* no oxalic acid is formed. An explanation of *Johnstone's* error may be found in *Berthelot's* observation, repeated by *Mangold*, that butyric acid yields oxalic acid when boiled for a considerable time with an excess of potassium permanganate.

An excess of sulphurous acid must be carefully avoided, since in presence of hydrated peroxide of manganese, sulphurous acid oxidises the oxalic acid formed. This error is obviated by *Allen's* proposal to use sodium sulphite instead of sulphurous acid. If the hydrated peroxide be removed by filtration, and the solution be acidified with acetic acid, no action on the oxalic acid takes place. But since towards the end of the washing small quantities of the peroxide pass through the filter, and are reduced by the sulphurous acid set free by the acetic acid, and, moreover, since small quantities of calcium sulphite may be admixed with the precipitated calcium oxalate, it will be best to avoid the use of sulphurous acid or of a sulphite altogether.

Herbig[4] substitutes, therefore, for the sulphite, hydrogen peroxide; he further recommends the use of a smaller quantity of potassium permanganate. *Herbig's* method has been examined by *Mangold*,[5] and the following modification of the *Benedikt-Zsigmondy* process has been recommended by him as yielding reliable results:—2-4 grms. of fat are saponified; the filtrate from the liberated fatty acids is made up to 300 c.c., placed in a litre flask, and 10 grms. of potassium hydrate, and as much of a 5 per cent permanganate solution as will correspond to *one and a half* times the theoretical quantity required for the oxidation of the glycerol (6·87 parts of MnO_4K being the amount required by theory for *one* part of $C_3H_8O_3$) are added. This operation is conducted in the *cold* and with constant shaking. Allow to stand for half an hour at the ordinary temperature, and add sufficient hydrogen peroxide (avoiding, however, a large excess) to completely decolourise the liquid. Then make up to 1000 c.c., shake well, and filter 500 c.c. through a dry filter. Boil the filtrate for half an hour to decompose all hydrogen peroxide, allow to cool to 60° C., acidify with sulphuric acid, and titrate with standard permanganate solution. In a recent publication *Herbig*[6] points out that cork and india-rubber connections in the apparatus should be avoided as they give rise to the formation of some oxalic acid.

If the glycerol solution obtained from the fat contains any other substance yielding oxalic acid on oxidation, as notably in the case of highly oxidised linseed oil, the *Benedikt-Zsigmondy* process is, of course,

[1] *Journ. Soc. Chem. Ind.* 1891, 204. [2] *Ibid.* 1891, 201
[3] *Ibid.* 1891, 803. [4] *Inaugural Dissertation.* Leipzig, 1890.
[5] *Journ. Soc. Chem. Ind.* 1891, 803. [6] *Chem. Rev.* 1903, V.

useless. In the preparation of the glycerol from the commercial oils and fats, the glycerol solution will always be more or less contaminated with impurities which may, or may not, lead to the formation of oxalic acid. This uncertainty robs the permanganate method to some extent of its usefulness.

Still more uncertain are the methods based on the oxidation of glycerol with potassium permanganate in acid solution when the glycerol is burnt up to carbon dioxide and water, according to the following equation :—

$$C_3H_8O_3 + 7O = 3CO_2 + 4H_2O.$$

If chemically pure glycerol be used the method would, of course, lead to correct results ; but in all other cases they will be so misleading that I consider it unnecessary to describe the methods that have been proposed under this head.[1]

For, whereas in the *Benedikt-Zsigmondy* method erroneous results are only obtained in the presence of organic substances yielding oxalic acid, oxidation in acid solution must lead to increased errors, since any other organic substance present will also yield carbonic acid and therefore render the determination practically useless.

Identical in principle with the last-named methods are the processes based on the oxidation of glycerol by means of potassium bichromate. Since the employment of potassium bichromate readily admits of the application of volumetric methods, oxidation by means of potassium bichromate has been recommended by several chemists.

A process of this kind is in use—for want of a better method —in the commercial determination of glycerol in soap lyes (see chap. xv.).

Other oxidising agents have been proposed by *Chaumeil*—iodic acid —and by *Gailhat*—permanganate in presence of manganese sulphate. The same strictures apply to these methods (*Lewkowitsch*[2]).

(2) *Determination of Glycerol by the Acetin Process*

Since in the saponification of a fat more or less impure glycerol is necessarily obtained, *Lewkowitsch*[3] recommends to prepare crude glycerin in a similar manner to that obtained on a large scale, and to determine accurately the proportion of glycerol by the *Benedikt-Cantor*[4] acetin process.

Twenty grams of an oil or fat are saponified in the usual way, and the alcohol driven off on a water-bath. The resulting soap is

[1] See second edition of this work, p. 211. [2] *Analyst*, 1903, 107.

[3] *Chemiker-Zeitung*, 1889, 659.

[4] *Journ. Soc. Chem. Ind.* 1888, 696 ; cp. also Lewkowitsch, *ibid.* 1889, 574 ; *Chem. Zeit.* 1889, 13, 93, 191, 659 ; Hehner, *Journ. Soc. Chem. Ind.* 1889, 6.

then decomposed with sulphuric acid and the liberated fatty acids are filtered off. The filtrate is neutralised with an excess of barium carbonate and boiled down on the water-bath until most of the water is driven off. The residue is exhausted with a mixture of ether and alcohol, the ether-alcohol driven off for the most part by gently heating on the water-bath, and the residue dried in a desiccator and weighed. It is not necessary to dry until constant weight is obtained, since the actual glycerol is determined in the crude product by the acetin method.

This process is based on the quantitative conversion of glycerol into triacetin (p. 271), when concentrated glycerol is heated with acetic anhydride. If the product of this reaction is then dissolved in water, and the free acetic acid has been carefully neutralised with alkali, the dissolved triacetin can be easily estimated by saponifying with a known volume of standard alkali and titrating back the excess. The solutions required are—

1. Half-normal or normal hydrochloric acid (*accurately standardised*).

2. Dilute caustic soda, containing about 20 grms. of NaOH in 1000 c.c. Its strength need not be known accurately.

3. A 10 per cent solution of caustic soda.

Solutions 2 and 3 are best kept in large bottles connected by means of syphon tubes with burettes, so that the filling of the latter may take place automatically. To prevent absorption of carbon dioxide from the air, the bottles are provided with soda-lime tubes through which the air has to pass.

The estimation of the glycerol is carried out as follows:—

About 1·5 grms. of the crude glycerin weighed off accurately are heated with 7-8 c.c. of acetic anhydride and 3 grms. of anhydrous sodium acetate (dried previously in an oven) for $1\frac{1}{2}$ hours in a round-bottomed flask, of about 100 c.c. capacity, connected with an inverted condenser. The mixture is then allowed to cool a little, 50 c.c. of warm water are poured down through the tube of the condenser, and the acetin made to dissolve by shaking the flask; if necessary, the contents of the flask may be slightly warmed, but must not be boiled. As triacetin is volatile with water vapours, these operations must be carried out whilst the flask is still connected with the condenser. The solution is next filtered from a flocculent precipitate, containing most of the impurities of the crude glycerin, into a wide-mouthed flask of about 500-600 c.c. capacity, and the filtrate allowed *to cool down* to the ordinary temperature. Phenolphthalein is then added, and the free acetic acid neutralised with the dilute caustic soda solution. Whilst running in the soda the solution must be agitated continually, so that the alkali may not be in excess locally longer than is unavoidable. The point of neutrality is reached when the slightly yellowish colour of the solution just changes into reddish-yellow. If the solution is allowed to become pink, the point of neutrality has been exceeded, and a fresh test must be made; the excess of soda cannot be titrated back, as partial saponification of the acetin takes

place in presence of the slightest excess of alkali. The change of colour is very characteristic, and is easily noticed after some little practice.

25 c.c. of the strong soda solution are now run in and the solution boiled for a quarter of an hour; the excess of soda is then titrated back with the standard acid. Side by side, operating in the same manner, 25 c.c. of the strong caustic soda are boiled and titrated with acid. The difference between the two titrations corresponds to the amount of alkali required for the saponification of the triacetin. From this the quantity of glycerol in the sample can be calculated, as shown in the following example:—Suppose 1·324 grms. of the sample have been treated as described above. Let 25 c.c. of the strong alkali require 60·5 c.c. of normal hydrochloric acid, and let the number of c.c. required for titrating back the excess of soda in the sample be 21·5 c.c., then $60·5 - 21·5 = 39·0$ c.c. have been used. 1 c.c. of normal acid corresponds to $\frac{0·092}{3} = 0·03067$ grms. of glycerol. Hence the sample contained $0·03067 \times 39 = 1·1960$ grms. or 90·3 per cent of glycerol.

The percentage found is then calculated to the crude glycerin obtained on saponifying the original quantity of 20 grms.

(3) *Determination of Glycerol as Isopropyliodide*

Zeisel and Fanto[1] proposed to determine glycerol by converting it into isopropyliodide. The method is based on the reaction expressed by the following equation:—

$$C_3H_5(OH)_3 + 5HI = C_3H_7I + 3H_2O + 2I_2.$$

The glycerol is converted, by means of hydriodic acid of spec. grav. 1·7 (even 1·9) into isopropyliodide, and the latter distilled over into an alcoholic solution of silver nitrate. The iodine which is formed at the same time is retained by red phosphorus. From the silver nitrate solution silver iodide is precipitated, and weighed as such, and each molecule of AgI is calculated to one molecule of glycerol.

The test is carried out in a special apparatus. The writer[2] has made two series of experiments on crude glycerine, but the results were found so much below the truth that the method cannot be recommended.

3. Diglycerides and Monoglycerides

The occurrence of lower glycerides in a fat has hitherto been proved in a direct manner in the solitary case of "rape oil stearine," dierucin having been isolated from a rancid rape oil (cp. chap. i. p. 4).

[1] *Zeit. f. d. landwirthsch. Versuchswesen in Oest.* 1902.
[2] Lewkowitsch, *Analyst*, 1903, 108.

It has been shown (cp. chap. i.) that we may expect the presence of di- and monoglycerides in oils and fats containing small quantities of free fatty acids. I have demonstrated this to be the case by proving, in an indirect manner, the occurrence of di- and monoglycerides in partially saponified oils and fats (chap. ii. p. 36).

To detect di- and monoglycerides in an oil or fat, I boil an *accurately weighed quantity of the sample with acetic anhydride*, and wash the resulting product with boiling water until it is freed from acid. In the presence of notable quantities of di- and monoglycerides an increase of weight will be found. This is due to one or two acetyl groups having been taken up respectively by one molecule of diglyceride or monoglyceride, as shown by the following equations :—

$$1.\quad C_3H_5{}^{OH}_{(OR)_2} + (C_2H_3O)_2O = C_3H_5{}^{O\,.\,C_2H_3O}_{(OR)_2} + C_2H_4O_2.$$

$$2.\quad C_3H_5{}^{(OH)_2}_{OR} + 2(C_2H_3O)_2O = C_3H_5{}^{(O\,.\,C_2H_3O)_2}_{OR} + 2C_2H_4O_2.$$

If the quantitative estimation be carried out with due care, in the case of a *pure diglyceride or monoglyceride its molecular weight may* be calculated from the increase in weight. Thus, to take an example, if a grms. of a pure diglyceride have been weighed off, and an increase of weight, i, has been found, we have the proportion

$$a : a + i = M : M + 42,$$

where M is the molecular weight of the diglyceride, and consequently M + 42 the molecular weight of the triglyceride obtained on assimilation of the group $C_2H_2O (= 42)$. The above proportion is expressed by the equation $a(M + 42) = M(a + i)$, hence

$$M = \frac{42a}{i}.$$

As a rule, however, the diglyceride will only form a small proportion of the fat under examination. If the chemical composition of the diglyceride be known, the absolute quantity of the diglyceride in the sample may be calculated with the help of the equation

$$a = \frac{Mi}{42}.$$

Thus if b grms. of a fat, containing a diglyceride a of the known molecular weight M, have been weighed off, and the increase i was obtained on acetylating, the percentage of the diglyceride in the sample will be found from the proportion

$$b : \frac{Mi}{42} = 100 : x,$$

hence

$$x = \frac{100Mi}{42b}.$$

The proportion of diglyceride can also be found volumetrically if the molecular weight of the diglyceride be known. If M be the molecular weight of the diglyceride, K the saponification value of the sample under examination, and C the saponification value of the acetylated product, then the percentage D of the diglyceride may be calculated from the following formula (56·1 being the molecular weight of KOH and 42 that of C_2H_2O):

$$D = \frac{100(C - K)M.(M + 42)}{56 \cdot 1(M - 84)},$$

at which I arrive as follows: M grms. of a diglyceride require $2 \times 56 \cdot 1$ grms. of KOH for saponification; M + 42 grms. of the triglyceride, obtained from it on digestion with acetic anhydride, require $3 \times 56 \cdot 1$ grms. KOH. Therefore 1 grm. of the diglyceride requires $\frac{2 \times 56 \cdot 1}{M}$, and 1 grm. of the triglyceride $\frac{3 \times 56 \cdot 1}{M + 42}$.

The difference

$$\frac{3 \times 56 \cdot 1}{M + 42} - \frac{2 \times 56 \cdot 1}{M} = \frac{56 \cdot 1(M - 2 \times 42)}{M(M + 42)}$$

will, for a sample consisting of a pure diglyceride, be practically equal to C - K, hence

$$D = \frac{100(C - K)M.(M + 42)}{56 \cdot 1(M - 2 \times 42)}.$$

Thus if the proportion of dierucin, $C_3H_5 \begin{matrix} \diagup (O_2C_{22}H_{41})_2 \\ \diagdown OH \end{matrix}$ (M = 732) in rape oil stearine has to be determined, and K be found = 158·4 for this rape oil stearine, and for the acetylated rape oil stearine C = 180·2, we have, since C - K = 21·8,

$$D = \frac{100 \times 21 \cdot 8 \times 732 \times 774}{56 \cdot 1 \times (732 - 84)} = 34.$$

The correctness of this calculation may be proved as follows:—

The saponification value of pure dierucin $C_3H_5(OC_{22}H_{41}O)_2(OH)$ is 153·3, that of acetylated dierucin $C_3H_5(OC_2H_3O)(OC_{22}H_{41}O)_2$ is 217·4. The difference 217·4 - 153·3 = 64·1; found C - K = 21·8; therefore

$$D = \frac{21 \cdot 8 \times 100}{64 \cdot 1} = 34.$$

In case the amount of free fatty acids in an oil or fat is considerable, anhydrides of the fatty acids may be formed, causing a decrease in weight; this decrease may, however, be obliterated by a simultaneous increase due to the presence of small quantities of lower glycerides.

Since complete hydrolysis of the anhydrides formed in the acetylating process is not obtained readily, it is necessary to remove the free fatty acids, if their amount be considerable, by converting them into potassium salts by titration with standard alkali, using

phenolphthalein as an indicator, and extracting the glycerides with ether.

If the free fatty acids contain soluble fatty acids, whilst the amount of total free fatty acids is at the same time inconsiderable, then it is necessary to wash the sample with hot water until the soluble fatty acids have been removed.

It should be distinctly understood that the above-given calculations hold good only in the absence of free fatty acids and of monoglycerides.

Since glycerides of hydroxylated fatty acids assimilate the acetyl group on being digested with acetic anhydride, it is necessary, in the presence of such glycerides, to prepare the insoluble fatty acids and determine their acetyl value. Thus the difficulty caused by the presence of lower glycerides is removed.

From the acetyl value of the fatty acids a measure of the hydroxylated acids is obtained (chap. viii. p. 368), and by introducing the most likely molecular weight, their absolute weight can be obtained and calculated to glycerides.

Oils and fats containing notable quantities of mono- and diglycerides furnish lower *Hehner* values and higher saponification values than their corresponding triglycerides. This will be seen by reference to the tables giving the respective values for monoglycerides and diglycerides.

When the oils and fats are acetylated, the decrease in the *Hehner* value becomes still more pronounced, whilst the saponification values, rise, as will be seen from the following table, in which I collate the corresponding values for the three most important mono- and diglycerides :—

[TABLE

Glyceride of Acid.	Acetylated Monoglyceride.				Acetylated Diglyceride.				Triglyceride.			
	Formula.	Molecular Weight.	Saponification Value.	Insoluble Fatty Acids. Per cent.	Formula.	Molecular Weight.	Saponification Value.	Insoluble Fatty Acids. Per cent.	Formula.	Molecular Weight.	Saponification Value.	Insoluble Fatty Acids. Per cent.
Palmitic	$C_3H_5(O.C_2H_3O)_2$ $O.C_{16}H_{31}O$	414	406·6	61·83	$C_3H_5(O.C_2H_3O)$ $(O.C_{16}H_{31}O)_2$	610	276·0	83·92	$C_3H_5(O.C_{16}H_{31}O)_3$	806	208·8	95·29
Stearic .	$C_3H_5(O.C_2H_3O)_2$ $O.C_{18}H_{35}O$	442	380·8	64·26	$C_3H_5(O.C_2H_3O)$ $(O.C_{18}H_{35}O)_2$	666	252·7	85·28	$C_3H_5(O.C_{18}H_{35}O)_3$	890	189·1	95·73
Oleic .	$C_3H_5(O.C_2H_3O)_2$ $O.C_{18}H_{33}O$	440	382·4	64·07	$C_3H_5(O.C_2H_3O)$ $(O.C_{18}H_{33}O)_2$	662	254·3	85·18	$C_3H_5(O.C_{18}H_{33}O)_3$	884	190·4	95·70

However, for practical purposes we cannot, as a rule, derive distinct indications from the Hehner values and the saponification values, since in the presence of small quantities of mono- and diglycerides the differences may fall within the errors of the method.

The same strictures would apply in a more forcible manner to the formula given by *Freundlich*[1] for the calculation of the proportion of diglycerides in oils and fats containing hydroxylated acids or their glycerides, without having recourse to the acetylating process. The use of this formula would lead to unjustified assumptions and conjectures if, in consequence of unavoidable errors, somewhat low values are found; this would notably apply to the "*Hehner* value," owing to the experimental errors attaching to this method. Hence I omit here *Freundlich's* formula.[2]

4. Unsaponifiable Matter

The term "unsaponifiable matter," like many terms borrowed from practice, is somewhat ambiguous.

I comprise here in the term "unsaponifiable matter" all those substances that are insoluble in water or do not combine with caustic alkalis to form soluble soaps. Strictly speaking, glycerol itself, not being saponifiable by alkalis—in the same way as wax alcohols—is "unsaponifiable," and in this strict sense only the fatty acids are, completely saponifiable, but not so the neutral glycerides, containing, as they do, about 5 per cent of the glycerol-yielding radicle C_3H_2. However, as glycerol is soluble in water it does not fall under the head of "unsaponifiable matter," and, therefore, in a wider sense the neutral fats are considered as completely saponifiable.

Most oils and fats contain in their natural state small quantities of unsaponifiable matter which consists to a large extent of phytosterol in the case of vegetable oils and fats, and of cholesterol in the case of animal oils and fats. Besides these two characteristic bodies some other substances occur, the nature of which has not yet been fully ascertained.

Waxes, although hydrolysed completely on boiling with alcoholic potash, are in practice sometimes termed unsaponifiable, on account of their naturally yielding considerable quantities of "unsaponifiable" alcohols, insoluble in water (besides containing hydrocarbons).

Here we are only concerned with the isolation and quantitative determination of the unsaponifiable matter in the natural products. The further examination of the isolated unsaponifiable matter will be considered at length in Chapter IX.

Preparatory to the determination of the unsaponifiable matter, the oil or fat must be saponified as described under the heading "saponification value." Therefore, in many cases, it will be found

[1] *Chem. Zeit.* 1901, 1129.

[2] Cp. *Jahrbuch der Chemie*, 1900, 361; cp. also Table No. 13, *Laboratory Companion to Fats and Oils Industries*. Macmillan and Co.

convenient to combine the determination of the saponification value with that of the unsaponifiable matter. But as the amount required for the correct determination of the unsaponifiable matter is several times greater than that usually taken for the determination of the saponification value, it will depend on the quantity of material used in the saponification test whether it is feasible to combine the two determinations. If two or three separate determinations of the saponification value have been made, then the material will suffice for the correct determination of the unsaponifiable matter, for it is not safe to employ less than 5 grms. of a substance for this test.

The unsaponifiable matter will usually be found dissolved in the soap solution after saponification; if somewhat larger quantities than usual are present, the unsaponifiable matter will cause turbidity of the soap solution (emulsion), or even float on the top of it.

The separation of the unsaponifiable matter from the saponified mass is based on the ready solubility of the unsaponifiable matter in ether, petroleum ether, and other solvents, in contradistinction to the practical insolubility of the soap in these solvents, whether it be dissolved in water or dilute alcohol, or has been brought to the dry state. Thus, two kinds of processes suggest themselves, namely, either (1) to extract the aqueous soap solution with ether or other solvents, or (2) to treat the dry soap mass with solvents.

(1) *Extraction of the Soap Solution with Solvents*

The extraction of the unsaponifiable matter is effected by repeatedly shaking the saponified mass, dissolved in a sufficient amount of water, with ether or petroleum ether, and separating the two layers by means of a separating funnel. The small quantities of soap that pass into the extract are removed by washing the ethereal solution with water. *H. Schwarz*[1] and *Neumann*[2] have designed special apparatus for this purpose, but its employment for the purposes of fat analysis cannot be recommended.

Regarding the choice of the solvent, it is always *safer* to use common ether in preference to petroleum ether, although the former extracts in most cases larger quantities of soap than the latter. Thus *Lewkowitsch*[3] found in the case of shark liver oil and some kinds of whale oil that petroleum ether gave very capricious results, all of which were far too low, owing, no doubt, to the "unsaponifiable matter" from these oils being very sparingly soluble in petroleum ether,[4] whereas constant results were obtained when using common ether. Due attention must be paid to the fact that the solubility of soaps in ether and petroleum ether is increased by the presence of hydrocarbon oils and wax alcohols; in accurate analysis it is

[1] *Journ. Soc. Chem. Ind.* 1884, 649. [2] *Berichte*, 18 (1885), 3061.

[3] *Journ. Soc. Chem. Ind.* 1896, 14.

[4] Shukoff and Schestakoff (*Journ. Soc. Chem. Ind.* 1898, 805, 878) confirm this for cholesterol (in the case of bone fats) which is readily extracted by common ether, but not so readily by petroleum ether, especially when (as in Morawski and Demski's process) the soap solution contains alcohol.

therefore necessary, after evaporating off the solvent, to shake the extracted unsaponifiable mass with a little warm water, and to extract again with ether or petroleum ether. *Lewkowitsch*[1] recommends to incinerate the extract; a residue giving an alkaline reaction on treatment with a little water would point to the presence of soap in the unsaponifiable matter. By titration with an acid the amount of alkali is found and the soap approximately calculated.

If the soap solutions happen to be neutral, then on diluting them with water, slight hydrolysis will set in and "acid soaps," such as sodium bistearate (see chap. iii. p. 76), are formed. Such acid soaps are somewhat soluble in ether; it is therefore advisable, when using ether, to have the soap solutions strongly alkaline, that is, containing an excess of alkali. Petroleum ether, on the other hand, more readily dissolves alkaline soaps, whereas neutral soaps are almost insoluble in this menstruum.

Very often a distinct separation into two well-defined layers does not take place readily, emulsions being formed on shaking which require a very long time to separate, if, indeed, they separate at all, as notably in the case of wool wax. In such cases it will be found most convenient to add a little alcohol or glycerol after shaking, if ether has been used for extraction, and to impart a slight rotatory movement to the separating funnel without, however, agitating. In other cases addition of a little caustic soda will more readily produce the desired effect. If petroleum ether has been employed, the formation of emulsions is best avoided by adding to the alcoholic soap solution obtained on saponification not more than an equal volume of water.

Sometimes a flocculent layer will appear between the aqueous solution and the solvent. In the case of wool wax *Lewkowitsch*[2] has shown that these flocks consist of a soap formed from fatty acids of high molecular weight, which is insoluble in cold water. The appearance of this flocculent stratum, however, does not interfere with the correct estimation of the unsaponifiable matter.

Petroleum ether should not contain any hydrocarbons boiling above 80° C.; otherwise it will be found almost impossible to remove the last portions of the solvent without seriously vitiating the results. The commercial article sold as boiling below 170° F. should not be taken on trust. It is, therefore, imperative to fractionate the petroleum ether, using a good dephlegmating column, say *Young's*, and to discard any fractions boiling above 80° C. (cp. p. 147).

Considering the importance of the subject, I think it best to describe fully several methods for the estimation of the unsaponifiable matter, for the reliability of which I can speak from practical experience. On the whole, preference should be given to the first method, recommended by *Allen* and *Thomson*,[3] which I describe in an amplified form as regards details.

Saponify 5 grms. of the sample with 25 c.c. of alcoholic caustic soda, containing 80 grms. of NaOH in 1000 c.c., in a porcelain basin

[1] *Journ. Soc. Chem. Ind.* 1892, 139; 1896, 14. [2] *Ibid.* 1892, 136.
[3] *Chem. News*, 43, 267.

on a water-bath, and boil down to dryness. The resulting soap is dissolved in 50 c.c. of hot water, and transferred to a separating funnel of about 200 c.c. capacity, using about 20 to 30 c.c. of water for rinsing the dish. After cooling, add 30 to 50 c.c. of ether and shake the solution thoroughly. Addition of a little alcohol will accelerate the separation. The soap solution is then run off into another separating funnel and is again exhausted with fresh ether. The ethereal solutions are united, washed with a small quantity of water to free them from any dissolved soap, and transferred to a tared flask. The ether is distilled off on the water-bath, and the residue dried at 100° C. and weighed.[1]

Morawski and *Demski*[2] treat 10 grms. of the sample with 50 c.c. of alcohol and 5 grms. of caustic potash previously dissolved in a small quantity of water. The flask in which the fat is saponified is connected with an inverted condenser, and after half an hour's boiling 50 c.c. of water are added, and the mass allowed to cool. It is then transferred to a separating funnel and shaken out with petroleum ether. When the two layers have separated, the aqueous layer is drawn off as completely as possible, and the petroleum ether repeatedly washed with water, without, however, uniting the washings with the main soap solution. Instead of running the ethereal solution directly into the tared flask, it is first drawn off into another dry flask, and from this poured into the tared flask, when any drops of water will remain behind. The main soap solution is again extracted in the same way, and the petroleum ether added to the first portion. On distilling off the petroleum ether, the unsaponifiable matter will be left behind.

Spitz and *Hönig*[3] recommend washing the petroleum ether layer with 50 per cent alcohol instead of water, thus shortening the time required for the separation of the two layers. This suggestion will in many cases prevent the formation of troublesome emulsions.

(2) *Extraction of the Dry Soap with Solvents*

For the extraction of the dry soap ether cannot be recommended, as larger quantities of soap would be dissolved than in the foregoing processes. Therefore petroleum ether or chloroform or acetone are preferable.

Allen and *Thomson* operate as follows :—10 grms. of the sample are saponified in a porcelain dish of 5 inches diameter with 50 c.c. of an 8 per cent alcoholic caustic soda solution, by gently boiling on the water-bath with constant stirring until the soap commences to froth ; 15 c.c. of alcohol are then added, and the boiling continued until the soap is dissolved. Next 5 grms. of sodium bicarbonate are

[1] In the case of bone fat *Shukoff* and *Schestakoff* do not wash the ethereal solution, but evaporate down to dryness, neutralise the extract (containing presumably acid soaps) with standard alkali, phenolphthalein being the indicator, and exhaust again with petroleum ether.

[2] *Journ. Soc. Chem. Ind.* 1886, 179. [3] *Ibid.* 1891, 1039.

stirred into the mass, and 50-70 grms. of recently ignited pure sand mixed with it. After drying for twenty minutes in a water-oven, the mass is transferred to a Soxhlet apparatus, and extracted with petroleum ether, completely volatile below 80° C. The petroleum ether is then distilled off and the residue weighed.

Finkener[1] uses the following process, which is but a slight modification of that proposed by *Allen* and *Thomson*:—Heat 10 grms. of the sample for fifteen minutes on a water-bath with 50 c.c. of nearly normal alcoholic solution of caustic soda, add 5 grms. of dry sodium bicarbonate to convert the excess of caustic soda into carbonate, and heat on the water-bath until the alcohol has been driven off. Transfer the hot mass to a stoppered cylinder, allow to cool, and shake with 300 c.c. of petroleum ether for some time. Filter into a dry flask, distil off the bulk of the petroleum ether, pour the solution on to a watch-glass, and weigh after evaporating off the remainder of the petroleum ether. This method is especially applicable in case considerable quantities of mineral oils are admixed with fatty oils.

For the more complete extraction of the unsaponifiable matter from dry soap, *Ritter*[2] recommends to mix the soap previous to extraction with *ether* with common salt. The advantage of the salt lies not in offering a larger surface, so that it cannot be replaced by sand or paper. Evidently the salt acts as a dehydrating agent, preventing the soap from passing into the ethereal solution.

The methods described under (1) cannot be employed for the determination of alcohols and other "unsaponifiable" portions of beeswax, carnaüba wax, and other solid waxes, since not only are the alcohols sparingly soluble in the cold solvents, but the alkali soaps of the fatty acids are not readily soluble in water or even dilute alcohol. In these cases middle layers of flocculent matter are apt to be formed, consisting of soaps of fatty acids having high molecular weight in intimate intermixture with "unsaponifiable matter." These middle layers so persistently retain the alcohols, etc., that even frequent shaking out with solvents fails to extract their total amount. In such cases it is best to prepare insoluble soaps of the fatty acids by neutralising the saponified mass with acetic acid, using phenolphthalein as an indicator, and to precipitate with barium chloride or lead acetate. The precipitate is washed, dried, mixed with sand, and boiled out repeatedly with petroleum ether.

In the case of shark liver oil and some kinds of whale oil, examined by *Lewkowitsch*[3] very considerable quantities of soap were dissolved out together with the alcohol, so that petroleum ether is useless in these cases. For these substances one of the processes described under (1) must therefore be used.

The following table contains a list of the percentages of unsaponifiable matter found in the natural oils, fats, and waxes. As the amount of unsaponifiable matter depends to a considerable extent

[1] *Journ. Soc. Chem. Ind.* 1886, 457. [2] *Chem. Zeit.* 1901, 872.
[3] *Journ. Soc. Chem. Ind.* 1896, 14.

on the mode of preparation and extraction, its proportion will, of course, vary with different specimens of one and the same oil. Hence, the percentage of unsaponifiable matter in oils and fats must be looked upon as a variable. In the case of waxes, the amount of unsaponifiable matter will also vary. But it should be borne in mind that the greatest part of the "unsaponifiable" consists of the alcoholic part of the esters, which latter have a tendency to be constant in quantity—as evidenced by their saponification values—whereas only the smaller portion of the unsaponifiable, namely, the hydrocarbons, will vary.

Oil.	Class.	Group.	Unsaponifiable. Per cent.
Linseed	Drying oils		0·42-1·1
Tung			0·44
Candle nut			0·76
Stillingia			1·45
Cedar nut			1·3
Hemp seed			1·08
Poppy seed			0·43
Sunflower			0·31
Soja bean	Semi-drying oils	Cotton seed oil group	0·22
Maize (corn)			1·35-2·86
Wheat			4·5
Cotton seed			0·73-1·64
Sesamé			0·95-1·32
Curcas, purging nut			0·5-0·58
Croton			0·55
Ravison		Rape oil group	1·45-1·66
Rape (colza)			0·58-1·0
Arachis	Non-drying oils		0·54-0·94
Hazel nut			0·5
Olive			0·46-1·0
Elderberry			0·66
Castor		*Castor oil group*	0·33
Menhaden	Marine animal oils	Fish oils	1·6-2·2
Sardine			0·52-0·86
Japanese sardine			0·48-2·6
Herring			0·99-10·7
Stickleback			1·73
Cod liver		Liver oils	0·54-7·83
Haddock liver			1·1
Skate liver			0·97
Tunny liver			1·0-1·8
Shark liver			10·2
Ling liver			2·23

Oil.	Class.	Group.	Unsaponifiable. Per cent.
Seal	Marine animal oils	Blubber oils	0·38-1·4
Whale			0·92-3·72
Porpoise, body oil			3·7
Porpoise, jaw oil			16·4
Cramp fish			22·0-24·1
Neat's foot	Terrestrial animal oils		0·12-0·65
Egg			1·7
Fat.			
Mowrah seed	Vegetable fats		2·34
Shea butter			3·5
Macassar			3·12
Japan wax			1·1-1·63
Human, adult	Animal fats	Non-drying fats	0·33
Lard			0·23
Bone			0·5-1·8
Wax.			
Sperm oil	Liquid waxes		37-41
Arctic sperm oil			31·7-42·6
Carnaüba wax	Solid waxes	Vegetable waxes	55
Wool wax		Animal waxes	43·1-51·8
Beeswax			52-55·6
Spermaceti			51·5

CHAPTER VII

QUALITATIVE EXAMINATION OF OILS, FATS, AND WAXES

Besides the "quantitative reactions" we have a number of chemical reactions, which are usefully applied to the examination of oils and fats, such as the elaïdin test, oxygen absorption test, thermal tests, etc. Hitherto, they have not been worked out so fully as to admit of their being classed amongst the quantitative reactions, although some of them, especially the hexabromide test, are likely to attain to that rank. Meanwhile we must look upon them as preliminary tests, that can be usefully employed as sorting tests, especially for purposes of classifying the oils and liquid waxes.

Those reactions that are caused by foreign matters admixed with the oils, as small quantities of resins, colouring matters, etc., give, as a rule, less decisive results, the quantity and sometimes also the nature of those impurities varying considerably in different specimens of the same oil owing to the different processes adopted for their preparation and purification. All the so-called colour reactions fall under this category. In some special cases, however, the colour reactions give definite indications.

The following tests and methods will be considered in this chapter :—

(1) Elaïdin Test.
(2) Sulphur Chloride Test.
(3) Oxygen Absorption Test.
(4) Hexabromide Test.
(5) Thermal Reactions.
(6) Colour Tests.

1. Elaïdin Test

This test is based on the fact that olein is converted into the solid isomeric elaïdin by nitrous acid, whilst the glycerides of linolic, linolenic, and isolinolenic acids remain liquid under the same conditions. The non-drying oils yield therefore solid masses, whereas the semi-drying and the drying oils give more or less liquid products (cp. chap. i. p. 29, *Lidoff*).

The elaïdin test was proposed first by *Poutet* in 1819 for the examination of adulterated olive oil; his original directions have been modified by many experimenters. *Poutet's* test, as practised in the Paris Municipal Laboratory, is carried out in the following manner:—10 grms. of the oil under examination, 5 grms. of nitric acid of specific gravity 1·38 to 1·41, and 1 grm. of mercury, are placed in a test-tube, and the mercury dissolved by shaking continuously for three minutes. The mixture is then allowed to stand for *twenty minutes, when it is shaken again for one minute.* The behaviour of different oils after that time is recorded in the following table:—

Kind of Oil.	Consistence.
Olive oil	*Solidified after 60 minutes.*
Arachis oil	,, ,, 80 ,,
Sheep's foot oil	,, ,, 120 ,,
Sesamé oil	,, ,, 185 ,,
Colza oil	,, ,, 185 ,,
Linseed oil	Forms a red, dough-like scum.
Cod liver oil	Becomes doughy, red, and forms a scum.
Whale oil	Same appearance.
Hemp seed oil	Remains unchanged.

For mercury, copper may be substituted. 10 c.c. of oil are placed together with 10 c.c. of 25 per cent nitric acid and 1 grm. of copper wire in a test-tube, and allowed to stand. *Finkener* [1] recommends for 10 c.c. of oil 0·2 grms. of copper and 0·5 grms. of nitric acid of spec. gravity 1·2.

The various modifications of the elaïdin test have been discussed by *Archbutt*,[2] who has thoroughly examined them. His results point to the following conclusions:—

(1) That the test must be made at a temperature not lower than 25° C., and that the temperature must be uniform throughout the experiment.

(2) *That the length of time required for solidification is of far* greater importance than the ultimate consistence of the elaïdin formed.

Archbutt prepares and applies *Poutet's* reagent in the following manner:—18 grms. of *mercury are placed in a dry stoppered 50 c.c.* cylinder, and 15·6 c.c. of nitric acid of 1·42 spec. gravity are added from a burette. The nitrous acid is entirely absorbed with production of a green colouration; as long as the reagent retains its green colour it is fit for use. 8 grms. of the reagent are shaken up with 96 grms. of the oil in a wide-mouthed stoppered bottle, placed in water of the required temperature, and again shaken at intervals of ten minutes during two hours.

When tested in this manner, the more important oils may be arranged according to *Allen* [3] in four groups:—

[1] *Zeit. analyt. Chem.* 1888 (27), 534. [2] *Journ. Soc. Chem. Ind.* 1886, 304.
[3] *Commercial Organic Analysis*, ii. 58.

(*a*) *A solid, hard mass* is yielded by: Olive oil, almond oil, arachis oil, lard oil, sperm oil, and sometimes neat's foot oil.

(*b*) *A butter-like mass* is yielded by: Neat's foot oil, Arctic sperm oil, mustard seed oil, and sometimes by arachis, sperm, and rape oils.

(*c*) *A pasty or buttery mass, separating from a fluid portion*, is yielded by: sunflower oil, niger seed oil, cotton seed oil, sesamé oil, rape oil, cod liver oil, seal oil, whale oil, and porpoise oil.

(*d*) *Liquid products* are yielded by: Linseed oil, hemp seed oil, and walnut oil.

Archbutt has also experimented with a reagent prepared by passing dry sulphur dioxide into cold nitric acid of specific gravity 1·42. By this reagent cotton seed oil and rape oil also are solidified; the product yielded by pure cotton seed oil is red, that given by rape oil deep red; but 10 per cent of either of these oils in olive oil does not sensibly colour the white elaïdin yielded by the latter oil.

The hardest elaïdins are obtained from arachis oil, olive oil, and lard oil. The elaïdin test has been specially applied to the examination of olive oil.

The elaïdin test cannot, however, be made to serve as a quantitative reaction.[1] It has been shown by *Hübl* that the most serious errors may be committed, when an attempt is made to draw conclusions as to the composition of an oil from differences in the time required for the formation of elaïdin, and from observations of the consistency and colour of the solidified mass, since the mode of preparing the nitrous acid, the mode of mixing the acid and oil, the shape of the vessel, and chiefly the temperature, influence the results to a very considerable extent.[2] Nor should it be forgotten that the age of an oil and the manner in which it has been kept (exposure to air and light) have an important bearing on the results of the elaïdin test. Thus *Gintl* has shown that an olive oil after exposure to sunlight for a fortnight did not yield any elaïdin at all.

In order to obtain trustworthy results, it will be found indispensable to institute side by side with the oil under examination a test with standard oils of known purity under exactly the same conditions.

2. Sulphur Chloride Test

E. Bruce Warren states that *drying oils*, on treatment with sulphur chloride, S_2Cl_2, yield solid masses, insoluble in carbon bisulphide, whereas *non-drying oils* on the same treatment give soluble products. On this reaction he bases a mode of discriminating between drying

[1] Cp. Oleic Acid, p. 108.

[2] The same conclusions have been re-stated by Wellemann, *Journ. Soc. Chem. Ind.* 1891, 800.

and non-drying oils. He determines the amount of drying oils in mixtures of fatty oils in the following manner:—

The reagent employed is sulphur chloride, diluted with an equal volume of carbon bisulphide. The sulphur chloride is obtained from the commercial yellow sulphur chloride, or "chloride of sulphur," by *fractional distillation, rejecting the portion boiling below 137° C.* [The portions having a lower boiling point may be digested with a *moderate excess of sulphur and fractionated again.*] The sulphur chloride is mixed with an equal volume of carbon bisulphide; the reagent is kept in bottles closed by corks coated with paraffin wax. The exact quantity required for a test is withdrawn by means of a pipette. To perform a test, 5 grms. of the oil under examination are mixed in a porcelain crucible of about 120 c.c. capacity with 2 c.c. of the reagent and 2 c.c. of carbon bisulphide, and warmed on the water-bath, with constant stirring, until reaction sets in. The mass soon becomes hard. The product must be broken up with a glass rod as completely as possible, in order to allow thorough expulsion of the volatile substances, and is dried until constant weight is obtained. The appearance of the product, both before and after drying—especially its colour and consistency—should be noted. *The dried mass is then finely powdered and exhausted with carbon* bisulphide, the solution evaporated to dryness, and the residue weighed. The quantity of the insoluble portion is found by difference. [It should be noted that every trace of moisture must be rigorously excluded.]

Thus *Warren* obtained the following figures on examining poppy seed and linseed oils:—

5 grms. of	Solid Insoluble Product.	Liquid Soluble Product.
	Grms.	Grms.
Poppy seed oil gave .	6·46	1·96
Linseed oil ,, .	6·36	0·78

Warren's method is based on older observations made by *Rochleder*,[1] *Roussin*,[2] *Perra*,[3] and *Mercier*.[4] His results, however, do not agree with *Rochleder's* statement that olive oil, eminently a *non-drying* oil, yields an insoluble product, and are further contradicted by *Sommer*[5] and by *Henriques*.[6] The experiments carried out by the latter prove conclusively that there exists no relationship between the drying power of an oil and the proportion of sulphur chloride it requires to form a solid product.

Experiments undertaken by the writer (with a view to converting the sulphur chloride test into a quantitative reaction) prove the

[1] *Dingl. Polyt. Journ.* 111, 159.
[2] *Ibid.* 151, 136.
[3] *Ibid.* 151, 138.
[4] *Compt. rend.* 84, 916.
[5] German Patent, No. 50, 282.
[6] *Journ. Soc. Chem. Ind.* 1894, 47.

unreliability of *Warren's* statements, as shown by the following table :—

Oils and Fats treated with S_2Cl_2 ; *5 grms. of fat ; 2 c.c.* S_2Cl_2, *and 2 c.c.* CS_2 (*Lewkowitsch*).

A. *Product completely soluble in Carbon Bisulphide*

Class of Oil.	Kind of Oil.	Mass thickens after Minutes.
Liquid waxes	Sperm oil, No. 1	20
	Sperm oil, No. 2	45
	Arctic sperm oil, No. 1	45
	Arctic sperm oil, No. 2	55
	Arctic sperm oil, No. 3	30
Vegetable fats	Mowrah seed oil	Do not thicken.
	Palm oil	
	Palm nut oil	
	Cocoa nut oil	
Animal fats	Lard	
	Butter fat	
	Beef tallow	
	Mutton tallow	

B. *Products not completely soluble in Carbon Bisulphide*

Class of Oil.	Kind of Oil.	Solidifies after Minutes.		Soluble in CS_2.
		In the Cold.	On the Water-bath.	Per cent.
Drying oils	Linseed	10	2	14·4
	Tung	$1\frac{1}{2}$	...	...
	Hemp seed	11	...	9·2
	Poppy seed	21	...	10·6
Fish oils	Japan fish	9	...	12·4
Liver oils	Cod liver, pure	15	...	4·4
	Cod liver, rancid	$1\frac{1}{2}$	...	6·4
Blubber oils	Seal	11	...	4·4
	Whale	13	...	3·0
Semi-drying oils	Cotton seed	20	4	24·0
	Sesamé	21	..	18·4
	Colza	23	...	2·8
	Rape	12	2	4·2
	Croton	18	...	25·4
Non-drying oils	Peach	26	...	4·8
	Almond, sweet	27	...	4·0
	Almond, bitter	28	...	3·4
	Arachis	30	...	6·0
	Olive	22	4	4·2
	Castor	$\frac{1}{2}$	at once	3·8
	Sheep's foot	36	...	6·0
	Horses' foot	20	...	13·6
	Neat's foot	23	...	9·4
	Lard	10	...	15·0
	Tallow	12	...	29·8

I have further found a remarkable difference in the action of sulphur chloride on vegetable oils on the one hand, and on their mixed fatty acids on the other. Whereas in the case of the former the reaction takes place quickly with the formation of a solid product, the free acids react more slowly, yielding but semi-solid, viscous products.

The reaction that takes place, when sulphur chloride is allowed to act on oils, appears to consist in an absorption of the elements of sulphur chloride, much as iodine chloride is absorbed in *Hübl's* test. In fact, *Henriques* has shown that after treatment with sulphur chloride oils have a far lower iodine absorption value than before. *Ulzer* and *Horn*, and afterwards also *Henriques*, have proved that the products of reaction contain sulphur and chlorine in approximately the same proportion as sulphur chloride (S_2Cl_2). Thus, the action of sulphur chloride on oils appears to consist in the conversion of unsaturated fatty acids or their glycerides into saturated compounds. Further research will be required to show whether a separation of saturated from unsaturated glycerides can be effected by means of this reagent. In this connection the difference is remarkable between lard and tallow on the one hand and their "oleines" on the other.

Much light has been thrown on the rationale of the chemical reaction involved by researches of *C. O. Weber*.[1] Further information on that subject will be given under "Rubber Substitutes" (chap. xv.). For the thermal reaction with sulphur chloride, cp. p. 322.

3. Oxygen Absorption Test

The absorption of oxygen from the atmosphere has a very important bearing on the liability of oils to cause spontaneous combustion when spread in a finely divided state on fibrous organic substances (cp. "Wool Oils," chap. xv.) Furthermore, it is of very great importance for the industries of paint oils, boiled oils, and varnishes (cp. chap. xv.).

It has been pointed out already (p. 2) that the iodine absorption stands in close relationship to the absorption of oxygen, the latter being tantamount to the drying power. It has further been explained that the classification based on the iodine value includes the subdivision of the oils and fats into drying, semi-drying, and non-drying oils.

Although the extremes of these groups, as represented by linseed oil and olive oil, are sharply defined in that the former easily "dries up" to a solid substance on exposure to air, even at the ordinary temperature, whereas the latter remains comparatively unchanged under the same conditions, there exist so many gradations between these two extremes, that a sharp line of demarcation cannot be drawn. The gradual transition from the true drying oils to the decidedly non-drying oils admits of the interposition of an intermediate class of semi-drying oils, but as the process of drying with formation of a skin may occupy in some cases as much as several

[1] *Journ. Soc. Chem. Ind.* 1894, 11.

months, it is evident that a strict subdivision cannot be based on the more or less defined drying properties.

It should be noted that the distinction drawn here between *drying, semi-drying,* and *non-drying oils is based on the behaviour of* the oils at the ordinary temperature, for according to *Livache* all oils, even solid fats, are oxidised on exposure to air at higher temperatures (see below).

The foregoing notes may be illustrated in a general way by some comparative tests due to *Archbutt.*[1]

Kind of Oil.	Time required for a thin film to dry in air at 50° C. 0·1 grm. oil on a glass surface 7 sq. cm.
Linseed	About 12 hours.
Maize	,, 18 ,,
Cotton seed	,, 21 ,,
Curcas	,, 24-30 hours.
Rape	,, 48 ,,
Olive	More than 13 days.

The chemical changes taking place when oils are "drying" are but very imperfectly understood, and further experiments are required to elucidate this important question (cp. "Boiled Oil," chap. xv.). The drying properties of an oil seem to stand in direct ratio to the *proportion of glycerides of linolenic and linolic acids in the oil.* Therefore, in a general way, the rule holds good that the higher the iodine value the better will an oil dry (tung oil seems to form an exception, chap. xiv.). This satisfactorily explains the fact that even closely related oils, such as the oils of the rape oil group, behave differently when exposed to the atmosphere. It should, however, be borne in mind that oleic acid, although an unsaturated acid, possesses no drying properties. Therefore a direct proportionality between the quantities of oxygen and of iodine, which drying oils assimilate, cannot be established, inasmuch as two atoms of iodine absorbed should correspond to one atom of oxygen. Still, a certain proportionality does exist, as will be seen from the following table, in which the percentage of oxygen actually absorbed is compared, with the quantity of oxygen calculated from the iodine absorption value by multiplying the latter by $\frac{16}{254} = 0{\cdot}063$.

Kind of Oil.	Oxygen Absorption.	
	Determined by Weighing.	Calculated from iodine Value.
	Per cent.	Per cent.
Linseed	16·6-19·3	10·77-12·66
Hemp seed	13·4	9·324
Walnut	7·9	9·135
Poppy seed	6·8	8·28-9·01

[1] *Journ. Soc. Chem. Ind.* 1899, 347.

If a convenient method were known for the accurate determination of the oxygen which is absorbed during the drying process, it would be possible to class the determination of the drying power, or, as it might be called, of the "oxygen value," amongst the quantitative tests. Determinations made by earlier observers were done in a very unsystematic fashion, insufficient regard having been paid to such important factors as temperature, influence of light, moisture of the atmosphere, thickness of layer exposed, and age of the oil, etc.

The earliest experiments consisted in exposing different oils to the atmosphere, and ascertaining the increase of weight which had taken place after a certain lapse of time. The greater the gain in weight, the greater was considered to be the oxygen absorption power of the oil, or in other words, the greater the drying power of the oil. But the numbers thus obtained could only give limited information as to the oxidation which had taken place. For if an oil was exposed, as was usually the case in these earlier experiments, in dishes in a layer of, say, one centimetre thick, then a skin would first be formed on the top layer. This would prevent further access of the oxygen of the atmosphere to the oil, so that whilst the top layer might represent a completely oxidised oil, the layer immediately below would only be partly oxidised, due to diffusion of oxygen into that middle layer, and the bottom layer would represent a practically unchanged oil.[1] This can be readily verified by exposing linseed oil in a porcelain dish, in a layer of about one centimetre thickness, to the atmosphere. After about a week a dry skin will have formed on the top. On breaking the skin it will be found that the layer immediately below is still viscid, whilst the bottom layer is liquid. Hence, such tables as given by *Mulder*[2] and *Kissling*[3] are of limited value, and I therefore omit them here. Besides, they do not take into account that the ascertained increase of weight merely represents the algebraical sum of all the changes that have occurred, and that therefore the increase of weight cannot be identified with the absorption of oxygen. In the course of drying, other changes take place, such as the formation of volatile acids, also of carbon dioxide, which cause a loss, the amount of which is obliterated by the preponderance of the gain through absorption of oxygen.

Since the drying of an oil requires protracted length of time, attempts were made to accelerate the progress of drying by mixing with the oils finely divided lead (*Livache*[4]), or finely divided copper (*Hübl*; *Lippert*[5]). *Livache's* lead powder is prepared by precipitating a lead salt with zinc, washing the precipitate rapidly in succession with water, alcohol, and ether, and finally drying in a vacuum. The test is carried out as follows:—Spread about 1 grm. of the lead powder (or copper powder) weighed off accurately on a somewhat large watch-glass, in a thin layer, and allow to fall on to it from a

[1] Weger, *Zeit. f. angew. Chem.* 1898, 492, 507; *Chem. Revue*, 1898, 315.
[2] *Chemie der austrocknenden Oele*
[3] *Journ. Soc. Chem. Ind.* 1891, 778; 1895, 479.
[4] *Ibid.* 1886, 494.
[5] *Chem. Revue*, 1899, 67.

pipette 6 to 7 grms. (not more) of the oil to be tested, placing each drop separately on the lead powder (or copper powder), taking care that the drops do not run into one another. Then allow the watch-glass to stand at the ordinary temperature exposed to light.

In this process, linseed oil reaches the maximum absorption within a few days, whereas under ordinary conditions the same result is only arrived at after a much longer time has elapsed. *Livache* states that drying oils absorb the maximum quantity of oxygen after eighteen hours, or in some cases after three days, whereas non-drying oils do not gain in weight before the lapse of four or five days. *Weger*[1] condemns *Livache's* process, and recommends to employ larger quantities of lead, so that for 0·2 grm. of oil there should be taken at least 2 grms. of lead powder. But even in that case the results were not found to be satisfactory, as will be detailed below.

The following table gives a number of results obtained by *Livache's method.* There is added the gain in weight of the free fatty acids, since the free fatty acids, with the notable exception of cotton seed oil, behave in *Livache's* test much like their glycerides, so that their increase in weight corresponds to the gain in weight of the neutral oils.

Oxygen Absorption by Livache's Test

Kind of Oil.	Gain in Weight of 100 Parts					Observer.
	Of Oil after			Until Weight remained constant (*Tortelli* [2]).	Of Fatty Acids after 8 days.	
	2 Days.	3 Days. (*Jean* [2]).	7 Days.			
Linseed	14·3	...	...	...	11·0	Livache
Stillingia	8·72	...	12·45 (8 days)	...	...	,,
Walnut	7·9	...	...	...	6·0	,,
Poppy seed	6·8	...	...	...	3·7	,,
Cotton seed	5·9	...	...	...	0·8	,,
Beech nut	4·3	...	...	...	2·6	,,
Colza	0·0	...	2·9	...	2·6	,,
Rape	0·0	...	2·9	...	0·9	,,
Sesamé	0·0	...	2·4	...	2·0	,,
Arachis	0·0	...	1·8	...	1·3	,,
Olive	0·0	...	1·7	...	0·7	,,
Japan *fish*	...	8·194				
Menhaden	...	5·454				
Sardine	...	...	...	4·22		
Cod liver	...	6·383	...	5·43		
Whale	...	8·266	...	7·62		
Neat's foot	...	...	...	1·19		
Sperm	...	1·629				

In order to obtain more rapid oxidation *Bishop*,[3] following the method adopted in practice with paint oils, spreads the oil on precipitated

[1] *Chem. Revue*, 1898, 246.

[2] Allowed to stand for three days in a dry atmosphere (under a desiccator over sulphuric acid).

[3] *Journ. Pharm. et Chimie*, 1896, 55; *Journ. Soc. Chem. Ind.* 1896, 475.

silica, and adds a little manganese resinate obtained from the commercial product by extraction with petroleum ether or common ether. *Bishop* proceeds as follows: 5 to 10 grms. of the oil are placed in a dish and mixed on the water-bath with exactly 2 per cent of manganese resinate, until the latter is completely dissolved. Meanwhile 1 grm. of calcined precipitated silica is weighed out into a flat-bottomed dish, and 1·02 grm. of the resinated oil, drop by drop, by means of a pipette, is added. The mass is intimately mixed by means of a glass rod, carefully spread over the bottom of the dish so as to offer a large surface to the air, and then left at a temperature of 17°-25° C. in the case of drying oils, and at 20°-30° C. for other oils. The dish is weighed after six hours, and twice again in the twenty-four hours, a fresh surface being exposed after each weighing by stirring the mass. The maximum increase in weight, calculated to per cents, is termed by *Bishop* the "*degree of oxidation.*"

The following table contains the results obtained by *Bishop*:—

Oils.	Specific Gravity.	Absorption of Oxygen in Per Cent "Degrees of Oxidation."	Mean Values.
Linseed oil, French	0·9327	17·70-16·40 [1]	17·05
,, ,, River Plata	0·9304	15·45-15·00	15·20
Hemp seed oil	0·9287	14·55-14·30	14·40
Poppy seed oil, French	0·924	14·50-13·90	14·20
Walnut oil, French	0·924	13·70	13·70
Cotton seed oil	0·924	8·60	8·60
,, ,, freed from stearine	0·923	9·60-9·30	9·45
Sesamé oil, Senegal	0·9215	8·95-8·50	8·70
,, ,, Indian	0·921	7·40	7·40
Arachis oil, African	0·916	6·70	6·70
,, ,, white	0·916	6·50	6·50
Colza oil, French	0·9142	6·40 (?)	6·40 (?)
,, ,, Indian	0·9137	5·90-5·80 (?)	5·85 (?)
Olive oil	0·9155	5·30 (?)	5·30 (?)

Fahrion [2] proposed to determine the oxygen absorption of oils by impregnating a strip of chamois leather with the oil under examination, and exposing it, suspended from a brass hook, to the atmosphere. Side by side with it is suspended a similar strip of leather, serving as a blank test, so as to eliminate the influence of evaporation of moisture from the leather, etc.

Fahrion's results are tabulated below; the absorption of oxygen has been calculated to per cents of oil used:—

[1] Lippert, *Journ. Soc. Chem. Ind.* 1898, 588, found in some cases, using comparatively fresh oils, the absorption from 17 to 18 per cent; in a few cases even 19 per cent, but never reaching 20 per cent.

[2] *Journ. Soc. Chem. Ind.* 1895, 811.

[TABLE

	Iodine Value.	Absorption of Oxygen in 100 parts of Oil after														Maximum.	Absorption according to Livache.	Calculated from the Iodine Value. I×0·063.
		1 Day.	2 Days.	3 Days.	4 Days.	5 Days.	6 Days.	7 Days	8 Days.	9 Days.	10 Days.	14 Days.	21 Days.	28 Days.	56 Days.			
Blank test.	..	0·0	1·0	1·3	0·0	1·4	−0·6	1·3	0·0	0·5	1·8	−0·5	1·1	3·3	−2·5	..	..	..
Olive oil . .	82·1	0·2	1·0	1·2	0·9	1·4	−0·4	1·1	−0·1	0·5	1·7	−0·5	0·7	3·5	−2·5	0·2	1·7	5·2
Sesamé oil .	110·2	0·1	1·2	0·9	0·5	1·1	−0·5	1·0	0·0	0·7	2·0	1·1	4·7	6·6	−0·5	3·6	2·4	7·0
Rape oil . .	102·4	0·1	1·1	1·3	1·0	1·8	0·5	2·5	2·0	2·8	4·6	2·3	3·2	6·3	−0·2	2·8	2·9	6·5
Cotton seed oil	109·2	−0·1	0·8	1·4	1·2	3·1	2·2	5·0	4·7	5·7	7·4	2·5	1·6	5·2	−1·4	5·6	5·9	6·9
Poppy seed oil	135·9	0·3	2·0	3·2	4·3	7·1	7·3	9·7	7·0	7·3	8·0	3·3	2·7	6·7	−0·3	8·4	6·8	8·6
Walnut oil .	149·2	−0·2	2·0	4·4	7·1	9·7	8·4	9·6	7·2	7·3	8·3	4·0	4·2	8·4	−1·3	9·0	7·9	9·4
Linseed oil .	175·8	0·1	1·5	2·0	3·8	12·3	11·8	13·2	10·4	11·3	11·8	7·9	8·2	12·6	4·5	12·4	14·3	11·1
Cod liver oil .	171·0	−0·6	1·1	8·1	10·0	10·9	8·0	10·4	8·0	8·5	10·1	6·8	6·3	11·8	4·3	9·5	6·4	10·8

From the foregoing notes it will be gathered that the changes accompanying the drying of an oil are of a very complicated nature, and depend on a variety of factors, namely, the age of an oil, the action of oxygen it has undergone through exposure to the air previous to examination, length of time of exposure, thickness of layer, atmospheric conditions, temperature, and influence of light. Examination of the influence which each of these factors exercise to the exclusion of the others would obviously be beset with great difficulties, and has not been carried out hitherto in a systematic fashion.

The influence of the length of time on the determination of the drying power is illustrated by the following table :—

No. of Oil.	Weight of Oil. Grms.	Weight of Lead. Grms.	Gain in Weight of 100 parts after			
			1 Day.	3 Days.	6 Days.	9 Days.
1	3·246	1·012	14·4	15·7	unchanged	...
2	3·154	0·653	2·45	12·0	15·9	unchanged

The oil No. 1 must be considered the better drying, although both oils finally reach the same absorption of oxygen.

With regard to the influence of temperature, it has been so far established that at elevated temperatures the absorption of oxygen takes place at an increased ratio.

Livache showed that rape oil and olive oil behave like drying oils when they are kept at a sufficiently high temperature (120°-160° C. with or without previous treatment with litharge or manganese borate), and become finally transformed into a solid substance, viz. *Mulder's* "linoxyn" (see chap. xv.). Further experiments of *Livache* demonstrate that all fatty substances without exception, whether of vegetable or animal origin, even solid animal fats, can be converted into "linoxyn," the rapidity of the change depending on the temperature used and the previous treatment to which the fatty substance has been subjected.[1]

Recently *Weger*, as also *Lippert*, have undertaken a systematic study of the drying power of oils, by exposing them in a very thin layer on glass plates to the action of the atmosphere. It was found that glass could not be replaced by other materials, lighter in weight; thus celluloid, gelatin, and even ebonite have been found completely useless. Sheets of mica, although useful for the work, are too easily damaged, and even sheets of thin metal have the drawback of being too easily creased. Necessary precautions in this test are: the glass must be perfectly clean, free from dust, and the oil must be spread with the greatest possible care in an evenly thin layer. If the layer is of uneven thickness, increase of weight might occur at one place, whilst

[1] Cp. Fleurent, *Journ. Soc. Chem. Ind.* 1898, 652.

simultaneously loss of weight might already take place in the thinner layer. A series of experiments showed that the thinner the layer of oil exposed, the more rapidly is oxygen absorbed at the commencement of the experiment, but after twenty-four hours an equilibrium seems to set in. The thicker the layer the smaller is the increase, but if the layer is too thin, unreliable results will be obtained. The best conditions seemed to be reached by spreading the oil so that about 0·0005 grm. are used per square centimetre of a glass plate.

The table facing this page reproduces the results collated from *Weger's* observations.

It will be seen that the process is an extremely tedious one, and depends on the accuracy with which decimilligrams can be ascertained. Besides, the method does not yield absolute figures, and can only be used as a guide in comparative tests. It must, therefore, depend on certain circumstances whether this method should be applied. For if it is merely a question of discriminating between drying, semi-drying, and non-drying oils, then the iodine value will not only be the most readily ascertainable sorting test, but will at the same time furnish quantitative results, as has been explained already. It should, however, be remembered that the iodine value must not be accepted as tantamount to expressing the drying power, for the fish and liver oils absorb approximately as much iodine as the best drying oils, and yet are greatly inferior to the latter as regards the quantity of oxygen absorbed, and furthermore most materially differ from them, in that the fish and liver oils do not form a skin as does linseed oil. Fish and liver oils are, however, best differentiated from the drying oils proper by the hexabromide test.[1]

4. Hexabromide Test

In his work on unsaturated fatty acids, *Hazura* also studied the action of bromine on these acids (see chap. viii.). *Hehner* and *Mitchell* applied *Hazura's* suggestive method to the glycerides themselves, and worked out a process which offers a means of differentiating drying oils, as also fish and liver oils, from oils belonging to the semi-drying and blubber oils.

Hehner and *Mitchell*[2] dissolve 1 to 2 grms. of an oil in 40 c.c. of ether, to which a few c.c. of glacial acetic acid have been added, cool the solution in a corked flask to 5° C., and then add bromine drop by drop until the brown colouration remains permanent. After standing for three hours the liquid is filtered through a tube containing asbestos, and is washed successively with 5 c.c. each of chilled glacial acetic acid, alcohol, and ether. The residue is finally dried in a water-oven to constant weight.

[1] A paper, "On the Influence of Atmospheric Oxidation on the Composition and Analytical Constants of Fatty Oils," has been published recently by H. C. Sherman and M. J. Falk, *Journ. Amer. Chem. Soc.* 1903 [25], 711.

[2] *The Analyst*, 1898, 313.

	s.	9 Days.	11 Days.	13 Days.	15 Days.	17 Days.	20 Days.	26 Days.	29 Days.	42 Days.	54 Days.	
	r it.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	
1	Lease	...	...	...	...	...	...	...	...	...	...	1
2	·7	Decrease	...	...	...	...	...	...	...	...	...	2
3		...	...	...	...	...	...	...	...	...	...	3
4		...		...	...	...	...	...	...	...	...	4
5	T13·6	Decrease	...	...	...	...	...	...	...	...	...	5
6	[illegible]	Decrease	...	...	...	...	...	...	...	...	...	6
7		...	...	...	...	...	...	...	...	...	...	7
8		...	...	...	...	...	...	...	...	...	...	8
9	H	...	...	...	...	...	...	...	...	...	...	9
10	P	Decrease	...	...	...	...	...	...	...	...	...	10
11	R	...	...	...	...	...	...	...	...	...	...	11
12		...	...	6·6	7·7	...	...	...	...	8·0	...	12
13	Pe	...	6·8	7·1	7·1	...	7·4	8·6	10·5	...	...	13
14	Ol	...	3·1	3·6	...	4·2	5·2	...	...	...	...	14
15	Pa	0·6	...	0·8	...	1·8	...	...	...	...	1·2	15

Pe

Ec

The following are the theoretical numbers for brominated triglycerides, the fatty acids of which contain eighteen atoms of carbon.

	Formula.	Bromine. Per cent.
Hexabromostearin . .	$C_3H_5(C_{18}H_{29}O_2Br_6)_3$	62·28
Tetrabromostearin . .	$C_3H_5(C_{18}H_{31}O_2Br_4)_3$	52·23
Dibromostearin . . .	$C_3H_5(C_{18}H_{33}O_2Br_2)_3$	35·19

In order to illustrate the usefulness of this method, I may point to the fact that tung oil was found in my laboratory[1] to yield no hexabromides, whereas *Maquenne's* formula $C_{18}H_{30}O_2$ for the chief unsaturated fatty acid in tung oil required that hexabromides should be obtained. This apparent discrepancy has been satisfactorily explained by *Kametaka*[2] having established the formula of $C_{18}H_{32}O_2$ for elæomargaric acid.

Halphen slightly modified *Hehner* and *Mitchell's* method by employing the following brominating reagent:—28 volumes of glacial acetic acid, 4 volumes of nitrobenzene, and 1 volume of bromine. He mixes 0·5 c.c. of the sample with 10 c.c. of the reagent in a test-tube, and differentiates qualitatively between oils which (1) give no precipitate even after one hour's standing and forms a clear solution; (2) those which give no precipitate after one hour's standing, but furnish a slightly turbid solution; (3) those which become distinctly turbid and yield a precipitate; and (4) oils which become turbid and separate into two layers on standing. In this form the test yields no more definite information than the iodine absorption test (cp. "Marine Animal Oils," chap. xiv.).

It is, therefore, far better to carry out the test in its quantitative form as proposed by *Hehner* and *Mitchell*. The following table gives the amounts of the bromo-compounds of glycerides obtained from a number of oils. The numbers due to *Walker* and *Warburton*[1] have been determined in the writer's laboratory.

[1] *The Analyst*, 1902, 237. [2] *Journ. Chem. Soc.* 1903, 1042.

Kind of Oil.	Yield of Hexabromides from Glycerides. Per cent.	Observer.
Linseed oil, (iodine value 181)	23·14 ; 23·52	Walker and Warburton
,, ,, (iodine value 186·4)	24·17	Lewkowitsch
,, ,, (iodine value 190·4)	37·72	,,
Linseed oil	23·86-25·8	Hehner and Mitchell
Tung oil	nil	,,
,, ,, 1st sample	nil	Walker and Warburton
,, ,, 2nd sample	0·38 ; 0·39	,,
Candle nut oil	8·21 ; 7·28	,,
Walnut oil	1·42-1·9	Hehner and Mitchell
Poppy seed oil	nil	,,
Maize oil	nil	,,
Cotton seed oil	nil	,,
,, ,, ,,[1]	nil	Lewkowitsch
Brazil nut oil	nil	Hehner and Mitchell
Almond oil	nil	,,
Olive oil	nil	,,
Japan fish oil	21·14 ; 22·07	Walker and Warburton
Fish oil, deodorised	49·01 ; 52·28	,,
Cod liver oil	42·9	Hehner and Mitchell
,, ,,	35·33 ; 33·76	Walker and Warburton
Cod oil, Newfoundland	32·68 ; 30·62	,,
Shark liver	22	Hehner and Mitchell
,, ,,	21·22 ; 19·08	Walker and Warburton
Seal oil	27·54 ; 27·92	,,
Whale oil	25	Hehner and Mitchell
,, ,,	15·54 ; 16·14	Walker and Warburton
Sperm oil	2·61 ; 2·42	,,
,, ,,	3·72 ; 3·69 (after standing 48 hours)	,,

5. Thermal Tests

(a) *Thermal Reaction with Sulphuric Acid: Maumené Test*

Maumené[2] observed that, on mixing concentrated sulphuric acid with drying oils, a higher temperature was produced than is the case with non-drying oils, and he proposed therefore the sulphuric acid test as a useful reaction in the examination of fats.

Fehling, Casselmann, Allen, Archbutt, and others have confirmed *Maumené's* observation, and proved that comparable results may be obtained if the experiments are carried out under exactly the same conditions. It is therefore necessary to *always* use sulphuric acid of precisely the same strength (the acid must be kept carefully protected from access of air), to cool the oil and the reagent to exactly the same temperature before commencing the operation, and even to use the same vessel for each determination.[3] (*Archbutt*, however, thinks that it is unnecessary to work at some constant initial temperature.)

Maumené[4] found that sulphuric acid heated to 320° C., and used immediately after cooling, gave a temperature reaction different from that given by an acid that had not been so treated. This is due to

[1] Cooled.
[2] *Compt. rend.* 35 (1882), 572.
[3] *Journ. Soc. Chem. Ind.* 1891, 234.
[4] *Compt. rend.* 92, 721.

partial dissociation of the sulphuric acid having taken place. Since, according to *Lunge* and *Naef*, sulphuric acid of 99 per cent and 96 per cent of SO_4H_2 have the same specific gravity, it is best to ascertain the strength of the sulphuric acid by titration (*Archbutt*[1]).

The influence of the concentration of the acid on the result is shown in the following table due to *Archbutt* (cp. also below, *Thomson* and *Ballantyne's* table, p. 320):—

Kind of Oil.	Rise of Temperature observed with Acid containing per cent of SO_4H_2.						
	97·38	96·71.	95·72.	94·72.	93·75.	92·73.	91·85.
	°C.	°C.	°C.	°C.	°C.	°C.	°C.
Olive, genuine	43·25; 42·25	42	39	36·5	34·5	31	28; 29·25
Rape, genuine	63, 62	61	58	54	50·25	47	40·5; 43
Olive, impure	48·5; 48·5	47; 47·5	43·75; 44·25	40·75; 40·25	38·5; 39	35·5; 35·5	32·5; 32·5

It should also be noted that on using weak acid the rise of temperature is very slow.

Archbutt recommends the following method of operating:—50 grms. of the oil to be tested (weighed accurately to within 10 to 20 milligrms.) are placed in a beaker of 200 c.c. capacity. The bottle of acid and the beaker of oil are then placed in a large vessel of water until both liquids have acquired the same temperature, which should be about 20° C. The beaker containing the oil is then removed, wiped outside, and placed in a "nest" of cardboard, having hollow sides stuffed with cotton wool, or in a larger beaker lined with cotton wadding. A thermometer is then immersed in the oil, and the temperature having been read off, 10 c.c. of the concentrated sulphuric acid are rapidly withdrawn from the bottle with a pipette and run into the oil, the time allowed for the emptying of the pipette occupying one minute. During this time the oil should be stirred with the thermometer, and the stirring continued until no further rise of temperature is observed. The highest point is easily noticed, as the temperature remains constant for some little time before it begins to fall.

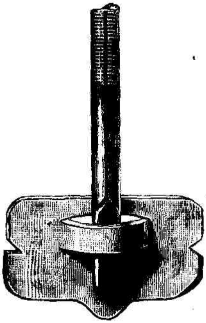


Fig. 36.

In order to secure a more perfect admixture of oil and acid, *Allen* fastens the thermometer to a tin plate, bent into the shape of a screw-paddle. This piece of apparatus, shown in Fig. 36, forms an efficient stirrer, producing a complete intermixture of the two liquids.

[1] *Journ. Soc. Chem. Ind.* 1886, 304.

The following table gives the rise of temperature by *Maumené's* test for various oils. The figures are arranged in the order of the magnitude of the iodine values, to show the correlation of the thermal reaction and the iodine absorbing power of the oils. The numbers given in this table are mean numbers obtained by different observers who worked under different conditions. Therefore the individual numbers given under the heading of each oil and fat in Chapter XIV. should also be consulted.

Oil.	Class.	Group.	Maumené Test. °C.	
Linseed	Drying oils		110-126	
Stillingia			136·5	
Cedar nut			98	
Garden rocket			126	
Hemp seed			97	
Walnut, nut			101-103	
Poppy seed			88	
Niger seed			81·5	
Sunflower			72	
Fir seed			98·5	
Madia			97	
Isano			115	
Mohamba			55	
Cameline	Semi-drying oils	Cotton seed oil group	82-117	
Soja bean			60	
Maize [corn]			81-86	
Kapok			95	
Beech nut			64	
Cotton seed			75-90	
Sesamé			65·5	
Brazil nut			51	
Curcas, purging nut			65-66	
Garden cress		Rape oil group	92-95	
Ravison			65-76	
Rape (colza)			55-64	
Black mustard			43	
White mustard			44-49	
Radish seed			51	
Jamba			52	
Cherry kernel	Non-drying oils		45	
Cherry laurel			44·5	
Apricot kernel			42-46	
Plum kernel			44·7	
Peach kernel			42·5	
Almond			52·5	
Sanguinella			52	
Acorn			60	
Californian nutmeg			77	
Arachis			45-51	
Pistachio			44·7	
Hazel nut			36	
Olive			41·5-45	
Coffee berry			54	

Oil.	Class.	Group.	Maumené. Test. °C.	
Grape seed . . . . Castor	Non-drying oils	Castor oil group	53 46-47	
Menhaden . . .	Marine animal oils	Fish oils	126	
Cod liver . . .		Liver oils	102-113	
Seal . . . . . Whale . . . . . Porpoise, body oil .		Blubber oils	92 92 50	
Sheep's foot . . . . Horses' foot . . . . Neat's foot . . .	Terrestrial animal oils		49·5 38 47-48·5	
Lard	Animal fats		24-27·5	
Waxes.				Specific Temp. Reaction.
Sperm oil . . . . Arctic sperm oil . .	Liquid waxes		51 41-47	100 93

There is undoubtedly a correlation between the rise of temperature in *Maumené's* test and the iodine value of an oil; the higher the temperature rises the higher is the iodine number (cp. chap. xiv. under "Olive Oil"). However, this correlation cannot be expressed by a constant factor, for *Hehner* and *Mitchell*[1] derived from

	Iodine number. / Maumené test.
9 observations made by one and the same observer, on lards, the factor	1·748
10 observations on olive oils, the factor	2·1837
203 observations on olive oils, the factor	2·314

Even on applying the last-named factor to other oils examined by the same observers, discordant results were obtained.

Oils exhibiting a very marked rise of temperature should be diluted, according to *Maumené*, with a measured quantity of olive oil. *Bishop*[2] recommends mineral oil for the same purpose, and calculates the rise of temperature, which the original oil would show, from the observed rise of temperature in the following manner (which, however, is not quite

[1] *Analyst*, 1895, 147. [2] *Journ. Phar. Chem.* 20. 302.

correct):—Let 67° C. be the rise of temperature obtained with 10 grms. of cod liver oil, 10 grms. of mineral oil, and 20 grms. of sulphuric acid; *if the rise of temperature of the mineral oil alone be* 14° C., then the figure for cod liver oil would be 2(67 – 14) = 106° C. (*Bishop*).

Bishop obtained in this manner the following results:—

Kind of Oil.	Rise of Temperature calculated. °C.
Cod liver, white	100
,, ,, pale	102
,, ,, brown	102·5
Arachis	66
Mixture consisting of 80 parts of cod liver oil, pale, and of 20 parts of arachis oil	97
Mineral oil	14

Ellis[1] also recommended mineral oil as a diluent. Having found that no concordant results were obtained when the maximum temperature was much over 60° C. (since above that temperature further reactions set in between sulphuric acid and the oil), *Ellis* considers it necessary to dilute each oil, if required, with mineral oil in such proportions that the highest temperature attained may be below 60° C. For his mode of calculation and his results the original paper must be consulted.

Jean[2] determines the heat evolved in *Maumené's* test by means of a special form of apparatus, styled by him "Thermelæometer." This apparatus (Fig. 37) consists of a small vessel, A, 4 cm. wide and 6 cm. high, graduated for the reception of 15 c.c. of oil, and of the acid holder B. The latter is fitted with a hollow glass-stopper C, to which is attached the india-rubber tube R. The neck of the acid holder is fastened to a clamp, to which a thermometer is fixed.[3]

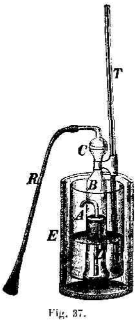


Fig. 37.

The mode of operating is as follows: 15 c.c. of oil, previously warmed to about 40° to 50° C., are placed in A, and 5 c.c. of concentrated sulphuric acid of specific gravity 1·819 are introduced into B. Vessel B is then placed in A, and the apparatus allowed to cool to 30° C., the thermometer being used to stir the oil occasionally. To prevent further cooling, A is placed in the felt-lined brass case E. The acid is then forced out of B through the small syphon-tube into A by blowing through R, and the mixture of oil and acid is well stirred until the maximum temperature is reached. Drying oils should be mixed with 5 c.c. of mineral oil.

[1] *Journ. Soc. Chem. Ind.* 1886, 150, 361. [2] *Ibid.* 1890, 113.

[3] Another apparatus, offering no special feature, has been used by Wiley (cp. Wiley, *Lard and Lard Adulterations*, Washington, 1889).

If the oils are much oxidised they must be treated with alcohol before testing; a better plan still is to prepare the fatty acids and test the latter. *Jean* has obtained the following results with his "*thermelæometer*":—

Kind of Oil.	Rise of Temperature of the	
	Neutral Oil. °C.	Fatty Acids. °C.
Linseed	61	109
Colza, French . . .	37	44
Colza, Indian . . .	37	46
Olive	41·5	45

The numbers obtained by *Jean* are, of course, not directly comparable with those given in the table.

Exposure to light and air with its concomitant oxidation increases the temperature reaction with sulphuric acid. Thus *Archbutt* records for a sample of olive oil, which, kept in the dark, gave a *Maumené* test of 41·5° C., the higher figure 52·5° C. after exposure.

This fact is brought out more prominently by *Ballantyne's* results:—

Kind of Oil.	Rise of Temperature.	
	Original Oil. °C.	*After Exposure.* °C.
Olive	41	67
Castor	73	78·5
Rape	61·5	72·5
Cotton seed	75·5	100
Arachis	73·5	90
Linseed	113·5	131

It should be noted that the reverse holds good for the iodine absorption numbers.

Thomson and *Ballantyne*[1] propose to refer the rise of temperature obtained with 50 grms. of oil and 10 c.c. of sulphuric acid to the rise of temperature which 50 grms. of water give under exactly the same conditions in the same vessel. The quotient $\frac{\text{Rise of temperature with oil}}{\text{Rise of temperature with water}}$ is termed by them "specific temperature reaction"; it expresses, therefore, the rise of temperature compared with water as unity. In the following table the results are multiplied by 100 in order to dispense with decimals. By recording

[1] *Journ. Soc. Chem. Ind.* 1891, 234.

the results in this way the discrepancies obtained on testing with sulphuric acids of varying strengths are, of course, considerably reduced, as will be seen from the following table :—

Kind of Oil.	Sulphuric Acid of 95·4 per cent.		Sulphuric Acid of 96·8 per cent.		Sulphuric Acid of 99 per cent.	
	Rise in Temperature. °C.	Specific Temperature Reaction.	Rise in Temperature. °C.	Specific Temperature Reaction.	Rise in Temperature. °C.	Specific Temperature Reaction.
Olive . .	36·5	95	39·4	95	44·8	96
Olive . .	...	...	39	94	43·8	94
Rape . .	49	127	...	...	58	124
Castor . .	34	88	37	89	...	...
Linseed . .	104·5	270	...	...	125·2	269
Water . .	38·6	100	41·4	100	46·5	100

The following specific temperature reactions are given by *Thomson* and *Ballantyne*, and by *Jenkins* : [1]—

[1] *Journ. Soc. Chem. Ind.* 1897 194.

[TABLE

Kind of Oil.	Specific Temperature Reaction. Water = 100. Thomson and Ballantyne.	Jenkins.	Class of Oil.
Japanese wood oil	...	330	Drying oils
Linseed oil, Baltic	349		
,, ,, East India	320		
,, ,, River Plate	320		
,, ,, raw	...	313	
,, ,, boiled	...	248	
Menhaden oil	306	...	Fish oils
Cod liver oil, medicinal	272	...	Liver oils
,, ,, Scotch	246		
,, ,, Newfoundland	243		
Seal oil	...	278	Blubber oils
,, ,, tinged	229		
,, ,, cold drawn, pale	225		
,, ,, Norwegian	223		
,, ,, steamed, pale	212		
Whale oil, pale	157		
Cotton seed oil, refined Egyptian	170	...	Semi-drying oils
,, ,, ,, ,,	169		
,, ,, *crude Egyptian*	163		
Ravison rape oil	...	162	
Rape oil	144		
,, ,,	135		
,, ,,	133		
,, ,,	...	130	
,, ,,	127		
,, ,,	125		
Castor oil, commercial	89	105	
Sperm oil, southern	100	...	Liquid waxes
Arctic sperm oil (Bottlenose)	93	103	
Arachis oil, commercial	137	...	Non-drying oils
,, ,, French, refined	105		
Olive oil, Malaga	94		
,, ,, Mogador	93		
,, ,, Mytilene	93		
,, ,, Syrian	93		
,, ,, commercial	92	94	
,, ,, Candia	92		
,, ,, Gioja	89		
Neat's foot oil	...	87	Animal oils
Blown cotton seed oil	...	164	Manufactured oils
Blown rape oil	...	153	

The writer has arranged the values in the order of their magnitude, and, as was to be expected, the same order obtains for the different classes of oils as in the table given above.

The *Maumené* test has been described here fully, as it has been largely used in this country and in the United States. It still seems to have a certain fascination for some workers, since even up to the present time investigations are being carried out. Thus *Mitchell*[1] has tried to instil new life into this test by an extended experimental research into the behaviour of glycerides and their fatty acids with concentrated sulphuric acid, carbon tetrachloride being used as a diluent in place of the diluents proposed by *Ellis* and other workers, as detailed above. Furthermore, *Sherman*, *Danziger*, and *Kohnstamm*[2] have published an extensive investigation of this test, paying especial attention to the influence of diluents and the effect of strength of acid. But since in my opinion the information derived from this test is incommensurate with the labour involved, and since much more definite information can be obtained by the application of the "quantitative reactions," it seems unnecessary to tabulate at length the results of the last-named chemists.

In the majority of examinations the analyst can very well dispense with this test altogether; especially since *Wijs'* modification of the *Hübl* test permits to ascertain the iodine value in a very short time, the *Maumené* test has lost almost entirely its significance. It will, therefore, only be used in rare cases, when the "quantitative reactions" fail to give a satisfactory and unambiguous answer.

Thus adulterations practised on olive oil may be detected with comparative ease, olive oil having the lowest rise in temperature with the exception of the animal oils. It may also offer some slight advantage in the examination of linseed oil for its drying power (cp. also "Lard," chap. xiv.), and perhaps also in the testing of the liquid unsaponifiable matter with a view to differentiate mineral, rosin, and tar oils. But in all these cases it is necessary to follow *Archbutt's* plan, *i.e.* every observer must construct a table for himself, using oils and fats of known purity, and whenever a sample is tested, compare the results with those furnished by the standard sample.

More reliable results, which can moreover be obtained in a much shorter space of time than the *Maumené* test, are furnished by the *Heat of Bromination Test* (cp. p. 325).

(*b*) *Thermal Reaction with Sulphur Chloride*

Fawsitt[3] proposed to measure the heat evolved by the action of sulphur chloride on various oils, with a view to discriminating between drying and non-drying oils, after the manner of *Maumené's* test (see p. 315). Since, however, this procedure offers no advantage over *Maumené's* test, or the bromination test (p. 325), it may suffice to

[1] *Analyst*, 1901, 169. [2] *Journ. Amer. Chem. Soc.* 1902, 266.
[3] *Journ. Soc. Chem. Ind.* 1888, 552.

briefly describe the *modus operandi*, and to record the values obtained in the table given below.

Thirty grams of the sample are weighed out in a small beaker, which is then placed in a larger beaker, the space between the two beakers being packed with cotton wool. A thermometer is inserted into the oil, the temperature observed, and the sulphur chloride poured in slowly, with constant stirring. The time is then taken, the thermometer kept stationary until the temperature ceases to rise, and both highest temperature and time noted.

Class of Oil.	Kind of Oil.	Number of c.c. S_2Cl_2 added.	Rise in Temperature.	Time in Rising.	Rise per Minute.	Final Condition of Oil.
			°C.	Min.	°C.	
Drying oils .	Linseed	2	57	5	11·4	Liquid, viscous
	,,	3	79	3	26·3	,, very viscous
	,,	4	97	2	48·7	Solid, sticky
Liver oils .	Cod liver	2	55	4	13·7	Liquid, viscous
	,, ,,	3	82	3	27·3	Solid, very sticky
	,, ,,	4	103	3	34·3	,, dry
Blubber oils .	Seal	2	45	10	4·4	Liquid, more viscous
	,,	3	79	6	13·2	Solid, sticky
	,,	4	112	5	22·4	,, dry
	Whale	2	57	6	9·4	Liquid, more viscous
	,,	3	71	5	14·1	,, very viscous
	,,	4	91	3	30·2	Solid, dry
Semi-drying oils	Cotton seed	2	49	11	4·4	Liquid, more viscous
	,,	3	64	9	7·1	,, very viscous
	,,	4	93	6	15·4	Solid, sticky
	Rape	2	53	10	5·3	Liquid, more viscous
	,,	3	66	7	9·3	Solid, slightly sticky
	,,	4	89	6	14·8	,, dry
Non-drying oils	Olive	2	52	6	8·7	Liquid, viscous
	,,	3	69	5	13·7	,, very viscous
	,,	4	94	4	23·5	Solid, dry
	Castor	2	56	2	27·7	Liquid, very viscous
Liquid waxes .	Sperm	2	37	16	2·3	Liquid
	,,	3	54	11	4·9	Liquid, more viscous
	,,	4	71	8	8·8	,, ,, ,,
	,,	5	86	6	14·2	,, very viscous
Animal oils .	Neat's foot	2	51	7	7·3	Liquid, more viscous
	,,	3	66	5	13·2	,, very viscous
	,,	4	82	4	20·5	Solid, sticky
	Lard	2	40	16	2·4	Liquid, very viscous
	,,	3	62	9	6·9	Solid, became dry on standing
	Oleic acid	2	53	6	10·6	Liquid, viscous
	,, ,,	3	74	5	14·9	,, ,,
	,, ,,	4	99	6	16·5	,, ,,
	Stearic acid	2	5 [1]	7	0·7	Solid
	,, ,,	4	8 [1]	5	1·6	,,
	Glycerol	4	21	7	3·0	Liquid

[1] Initial temperature.

(*c*) *Thermal Reaction with Bromine; Heat of Bromination Test. Bromine Thermal Value*

The action of bromine on oils and fats is attended with considerable evolution of heat. *Hehner* and *Mitchell*[1] proved by their researches that the measurement of the heat thus evolved leads to results furnishing more definite data than those obtained in the *Maumené* test.

Hehner and *Mitchell* proceed as follows:—

One gram of the oil under examination is placed in a *Dewar* vacuum-jacketed test-tube[2] and dissolved in 10 c.c of chloroform, the diluent being used to moderate the action. Exactly 1 c.c. of bromine, measured by means of a pipette (provided at its upper end with a narrow tube filled with caustic lime, and having an asbestos plug at each end), and previously brought to the same temperature as the oil in the vacuum tube, is run in, and the rise of temperature (due to the instantaneous reaction) is measured by means of a correct thermometer divided into fifths of a degree centigrade.

The whole operation occupies only a few minutes. Fatty acids are dissolved in glacial acetic acid instead of chloroform, and treated as above.

Hehner and *Mitchell* compared the numbers obtained for the rise of temperature of various oils and fats with their iodine numbers, with a view to elucidating the correlation, if any, existing between these two values. As will be seen from the following table, due to *Hehner* and *Mitchell*, the factor 5·5 serves to express the relation with considerable accuracy for the majority of the fatty substances examined by them under their particular conditions. The column headed "Deviation" has been added by the writer.

[1] *Analyst*, 1895, 148.

[2] The oil may be weighed in the tube, suspended obliquely, by means of platinum wire, from the arm of the balance. (Cp. Archbutt, *Journ. Soc. Chem. Ind.* 1897, 310.) In their earlier experiments *Hehner* and *Mitchell* employed an ordinary test-tube packed with cotton wool into a beaker; the results thus obtained are, *cæteris paribus*, two degrees centigrade lower.

[TABLE

I. Oil or Fat.	II. Heat of Bromination.	III. Iodine Number.		IV. Deviation.	
	°C.	Experiment.	Calculated from Column II. by multiplying by 5·5.	Absol.	Per cent.
Lard, No. 1	10·6	57·15	58·3	+1·15	+2·00
,, 2	10·4	57·13	57·2	+0·07	+0·12
,, 3	11·2	63·11	61·6	−1·51	−2·40
,, 4	11·2	61·49	61·6	+0·11	+0·18
,, 5	11·8	64·69	64·9	+0·21	+0·32
,, 6	11·8	63·96	64·9	+0·94	+1·50
,, 7	10·2	57·15	56·1	−1·05	−1·90
,, 8	10·4	57·80	57·2	−0·60	−1·05
,, 9	9·0	50·38	49·5	−0·88	−1·70
,, 10	11·0	58·84	60·5	+1·66	+2·7
,, +10 per cent cotton seed oil	11·6	64·13	63·8	−0·33	−0·52
Lard fatty acids	10·4	59·60	57·2	−2·40	−4·20
,, ,,	11·0	59·15	60·5	+0·35	+0·57
Mutton fat (kidney)	8·1	44·48	44·5	+0·02	+0·05
,, ,, (flare)	7·6	39·70	41·8	+2·10	+5·0
Butter, No. 1	6·6	37·07	36·3	−0·77	−2·1
,, 2	7·0	38·60	38·5	−0·10	−0·27
,, fatty acids	6·2	36·50	34·1	−2·40	−7·04
Almond oil	17·6	96·64	96·68	+0·04	+0·041
Olive oil	15·0	80·76	82·50	−1·74	+2·1
Maize oil	21·5	122·0	118·20	−3·80	−3·2
Cotton seed oil	19·4	107·13	106·70	−0·43	−0·4
Castor oil	15·0	83·77	82·50	−1·27	−1·5
Linseed oil, No. 1	30·4	160·7	167·20	+6·5	+3·9
,, ,, No. 2	31·3	154·9	172·00	+17·1	+10·0
Rape oil, No. 1	18·4	88·33	101·20	+12·87	+12·7
,, ,, No. 2	17·6	77·2	96·80	+19·6	+20·0
Cod liver oil	28·0	144·03	140·00	−4·03	−2·9
Commercial oil	19·0	108·5	104·5	−4·00	−3·8
,, ,,	19·2	105·7	105·6	−0·01	−0·009
,, ,,	18·9	105·7	103·9	−1·8	−1·7

It should be distinctly understood that the factor 5·5 must not be taken as an absolute one, but as depending on the particular vacuum-tube and the *modus operandi* adopted by *Hehner* and *Mitchell*. It is therefore imperative that each chemist using this method should ascertain the factor applying to his individual case by determining the heat of bromination of a non-drying oil, the iodine value of which has been ascertained by *Hübl's* method.

Thus *Jenkins*[1] obtained the constant factor 5·7, and *Archbutt*[2] found it to vary in the case of tallow, olive oil, rape oil, and linseed oil from 5·7 to 6·2. In the latter case the variation may be partly due to the fact that the weight of substance taken was not the same in every instance.

1 *Journ. Soc. Chem. Ind.* 1897, 194.
2 *Ibid.* 1897, 310. Cp. also Wilson, *Chem. News*, 1896, 27.

Notwithstanding the considerable differences shown in the case of linseed and rape oils, *Hehner* and *Mitchell* considered that the determination of the iodine number by *Hübl's* method may be replaced by that of the heat of bromination. They even went so far as to express the opinion that the *calculated* iodine values of linseed and rape oils examined are more correct than those found by *Hübl's* method. In the writer's opinion this is tantamount to begging the question, and a larger number of experiments is required to substantiate so far-reaching conclusions. This is all the more necessary as serious deviations have been stated by *Jenkins* for tung oil and for "blown oils."

On account of the exceeding simplicity of this test, and the rapidity in its execution, the heat of bromination test may prove a very useful auxiliary test, especially where a large number of specimens of the same kind have to be examined in a short time. It will be no less useful as a sorting test (*Hehner*), affording rapid information as to the class to which an oil belongs.

Its great rapidity being one of the chief recommendations in favour of using this test, *Wiley's*[1] modification (to employ a chloroformic solution of bromine) would seem to complicate matters, all the more so as a lowering of temperature takes place when bromine is dissolved in chloroform. The latter fact has already led to the suggestion to substitute carbon tetrachloride for chloroform. In the case of oils giving a violent reaction, as linseed oil, *Archbutt*[2] suggests to work with 0·5 grm. of oil, and to multiply the result by 2, and in the case of solid fats, which develop but little heat, to take 2 grms., and divide the result by 2.

6. Colour Tests

Various colour reactions have been proposed from time to time, and are still being proposed, for the recognition of oils.

A very complete synopsis of the older methods has been given by *Chateau* in his work *On Fats*.[3] The following tests, some of which are still being employed, may be mentioned in chronological order:—

Fauré (1839) stated that vegetable oils can be distinguished from animal oils by gaseous chlorine, the latter oils—with the exception of foot oils from terrestrial animals—becoming black on treatment with this reagent. The same chemist also employed ammonia as a general reagent.

Heydenreich (1848) first employed concentrated sulphuric acid for the examination of oils; his test consists in letting fall five drops of the oil under examination on the surface of pure concentrated sulphuric acid in a porcelain basin, and observing the colours developed during the first three minutes.

Penot introduced sulphuric acid saturated with potassium bichro-

[1] *Journ. Soc. Chem. Ind.* 1896, 384. [2] *Ibid.* 1897, 310.

[3] Chateau, *Die Fette, bearbeitet von H. Hartmann.* Leipzig. 1864.

mate as a general reagent, the various colours obtained with different oils being considered as characteristic for those oils.

Behrens used a mixture of equal parts of sulphuric and nitric acids.

Crace Calvert's (1854) method has for a long time been in vogue. This chemist examined the colour reactions noticeable on treating oils with the following reagents: (1) caustic soda, 1·340 spec. grav.; (2) sulphuric acid, 1·475 spec. grav.; (3) sulphuric acid, 1·530 spec. grav.; (4) sulphuric acid, 1·635 spec. grav.; (5) nitric acid, 1·180 spec. grav.; (6) nitric acid, 1·220 spec. grav.; (7) nitric acid, 1·330 spec. grav., and subsequently caustic soda, 1·340 spec. grav.; (8) syrupy phosphoric acid; (9) mixture of equal volumes of nitric acid, 1·330, and sulphuric acid, 1·345; (10) aqua regia, consisting of 25 measures of hydrochloric acid and 1 measure of nitric acid, 1·330, and subsequent treatment with caustic soda. In some text-books *Crace Calvert's* results are presented in a tabular form; for reasons stated below the table is omitted in this work.

Hauchecour-Yvetot proposed hydrogen peroxide as a general reagent.

Chateau, in his book *On Fats*, has published very extensive tables, in which an attempt is made to distinguish the oils by systematic application of the following reagents: (*a*) calcium polysulphide, (*b*) zinc chloride, (*c*) concentrated sulphuric acid, (*d*) fuming stannic chloride, (*e*) syrupy phosphoric acid, (*f*) phosphoric acid, (*g*) mercuric nitrate, with subsequent addition of sulphuric acid, (*h*) mercuric nitrate alone. All these tests must, on the whole, be considered of very little value, and are therefore not recorded here.

Later on *Glaessner* (1873) also proposed a systematic examination of oils, using as reagents caustic potash, fuming nitric acid, and concentrated sulphuric acid.

In order to avoid a rise of temperature with the last-mentioned acid, whereby some characteristic colour reactions may become indistinct, or the oil may become partially charred, *Finkener* dilutes the oils with carbon bisulphide. This solvent appeared to him suitable, as no thermal reaction takes place on mixing it with concentrated sulphuric acid.

All colour reactions must be used with the greatest caution, small quantities of resinoid or albuminoid substances, or other foreign matters, such as cholesterol, influencing the tints to such an extent that in most cases it will remain doubtful whether the reactions are really characteristic of the oils themselves. A notable example of a serious mistake of this kind was the reddish-brown colour obtained on treating imperfectly purified tallow with nitric acid being erroneously attributed to the presence of cotton seed stearine.

The colour reactions were chiefly resorted to for want of better methods; they have been in most cases superseded by the "quantitative reactions." It should be borne in mind that many colour reactions quoted in older text-books, and perpetuated in even more

recent treatises, were not always obtained with typical samples, little or no regard having been paid to their source, their age, their mode of purification, and all that host of circumstances that have a vital influence on the colour the reagents produce. In consequence of progress made in technical processes, a number of impurities, the very substances that gave origin to the colours supposed to be characteristic, have ceased to occur in commercial samples.

A colour reaction can only be of value if it be produced by a well-defined substance, naturally occurring in an oil or fat, and characteristic of it to such an extent that it may be identified by that reaction. Obviously, these characteristic substances occurring only in minute quantities should not be easily removable in the course of the usual manufacturing processes.

As a type of a most valuable reaction of this kind I refer to *Baudouin's* test for sesamé oil, which has found its scientific explanation and confirmation in the isolation of the colour-producing principle in that oil (cp. "Sesamé Oil," chap. xiv.). The colour reaction for cholesterol, although highly characteristic, requires more circumspection, as other substances also give the same or a very similar colouration.

Group reagents, such as are used in inorganic analysis, do not exist, and every new reagent recommended as such must be received with great suspicion.

The writer[1] has carefully examined four of the so-called group reagents, viz. concentrated sulphuric acid, gaseous chlorine, syrupy phosphoric acid, and phospho-molybdic acid. His experiments led him to the following conclusions :—

Sulphuric Acid.—This reagent enables, at best, with a good deal of practice, to discriminate between drying, semi-drying, and non-drying oils, if the acid be applied to the oil direct. The first-named oils may be recognised by their forming dark clots, when, say, two drops of concentrated acid are stirred into twenty drops of oil. A discrimination between semi-drying and non-drying oils, however, is more difficult and indeed scarcely possible in every case.

The better drying an oil is, the darker it will be coloured by the acid, so that it may be possible, judging from the depth of the colour, to distinguish between oils standing at the extreme ends of these classes, such as cotton seed oil and olive oil, whereas it is impossible to differentiate, by this test alone, *e.g.* rape oil from cotton seed oil. The colour reactions obtained with a solution of the oil in carbon bisulphide cannot be said to yield more reliable results, the dilution tending to obliterate the otherwise sharp distinction between the eminently drying and the other oils.

In the case of liver oils, the blue and purple colourations due to the presence of cholesterol and colouring principles—lipochromes—are very characteristic ; they are best observed if the oil is previously dissolved in carbon bisulphide. But the value of this test is greatly diminished by the fact that some blubber oils (perhaps due to an

[1] Lewkowitsch, *Journ. Soc. Chem. Ind.* 1894, 617.

accidental admixture with liver oils) show the same reaction. It should also be borne in mind that with the setting in of rancidity the chromogenetic substances are frequently destroyed.

Chlorine gas cannot be admitted as a group reagent for marine animal oils, the black colour being influenced by the state of purity and rancidity of the oil, so that even vegetable oils or terrestrial animal oils may give stronger colourations than pure liver oils.

Phosphoric acid appears to indicate only impurities that may be eliminated by refining, or products of oxidation or rancidity.

Phospho-molybdic Acid.—This reagent has been proposed by *Welmans.*[1] The test is performed as follows: 1 grm. (or 25 drops) of an oil or fat is dissolved in 5 c.c. of chloroform in a test-tube, and agitated with 2 c.c. of a freshly prepared solution of phospho-molybdic acid,[2] or of sodium phospho-molybdate and a few drops of nitric acid. After standing for a short time the chloroformic layer becomes colourless, whereas the upper layer shows, in the case of a vegetable oil and of cod liver oil, according to *Welmans*, a green colour. On adding ammonia or a fixed alkali a beautiful blue colour appears, the intensity of which corresponds to that of the green tint noticed before. Animal fats—with the above-mentioned exception of cod liver oil—were stated to cause no reduction, and consequently to produce no green with subsequent blue colouration.

The writer's experiments,[3] however, demonstrate that such a distinction cannot be upheld. Several kinds of olive oil, as also almond, arachis, and peach oils, showed far less distinct colours than tallow oil, and even lard oil. Amongst the large numbers of oils and fats of undoubted genuineness and belonging to all classes of oils and fats I have examined, only pure, freshly rendered lard left the phospho-molybdic acid unreduced, so that it remained colourless on being supersaturated with ammonia. But a slightly rancid lard behaved almost like a vegetable oil in *Welmans'* test. Moreover, mineral oil and rosin oil gave deep colourations; the phospho-molybdic acid test can, therefore, only rank amongst preliminary tests.

The green colour is due, according to *Welmans*,[4] to a mixture of the yellow reagent with the blue reduction product. If the yellow colour be taken away by adding ammonia, blue remains.

Special colour reactions, useful in some instances for the identification of an oil or for the detection of an adulterant, such as the *Halphen* test for cotton seed oil, will be exhaustively dealt with in the chapter treating of the distinctive properties of the individual oils and fats.

[1] *Journ. Soc. Chem. Ind.* 1892, 548.

[2] The reagent is prepared by precipitating a solution of ammonium molybdate with sodium phosphate, washing the precipitate thoroughly and dissolving it in a warm solution of sodium carbonate. The solution is boiled down to dryness and the residue heated. If the residue becomes coloured blue, add a few drops of nitric acid and heat again. Then boil the residue with water, add nitric acid until strongly acid, and dilute so as to obtain a 10 per cent solution. Filter if necessary and keep the reagent protected from dust.

[3] Lewkowitsch, *Journ. Soc. Chem. Ind.* 1894, 619.

[4] *Zeits. öffentl. Chem.* 6, 127.

CHAPTER VIII

EXAMINATION OF MIXED FATTY ACIDS

If the *quantitative and qualitative reactions* described in the two preceding chapters have led to insufficient information, or if it be desired to gain a further insight into the composition of the individual esters—glycerides in the case of oils and fats, or esters of *monohydric alcohols in the case of waxes—it becomes necessary to* examine the mixed fatty acids. In the case of glycerides the problem is somewhat simpler than in the case of waxes, as the basic constituent of all the glycerides—glycerol—can be easily removed after saponification has been carried out. A complication arises if we have to take into account a notable amount of soluble fatty acids, the presence of which is indicated by the high saponification value and the high Reichert-Meissl value of the sample. This case will be specially considered in Section 3 of this chapter.

The mixed insoluble fatty acids contain small amounts of unsaponifiable matter, as has been explained already (p. 266). If the unsaponifiable matter does not exceed 0·5 per cent or, at the most, 1 per cent, then it may, as a rule, be neglected, otherwise the *unsaponifiable matter must be separated from the soap solution before* the fatty acids are isolated. This becomes imperative in the case of waxes, the alcoholic constituents of which form about 50 per cent of the total mass. Their separation from the fatty acids is effected in the manner described already under "Unsaponifiable" in Chapter VI.

In the following sections an attempt is made to describe the methods applicable to the examination of the isolated fatty acids in a systematic manner, following, as far as possible, the order adopted in Chapter VI. Most of these methods admit of the estimation of the amounts of the constituents quantitatively, or approximately so. The methods embrace the determination of :—

1. The Neutralisation Value, from which the Mean Molecular Weight can be calculated.
2. Lactones—Anhydrides.
3. Soluble (volatile) Fatty Acids.
4. Saturated Fatty Acids in presence of Unsaturated Fatty Acids.
5. Saturated Fatty Acids.

6. *Oleic Acid in Admixture with Saturated Fatty Acids.*
7. Liquid Fatty Acids—Oleic, Linolic, Linolenic.
8. Hydroxylated Fatty Acids.
9. Oxidised Fatty Acids.

1. The Neutralisation Value—Mean Molecular Weight

The neutralisation value indicates the number of milligrams of potassium hydrate required to saturate one gram of the mixed fatty acids.

In the case of those oils and fats, the saponification values of which do not exceed considerably 195, the mixed fatty acids obtained either by the process described (chap. iii. p. 62), or under the heading "Hehner Value" may, for practical purposes, be considered as representing the total fatty acids contained in an oil or fat.

If, however, the saponification value of the sample exceeds 200, it is advisable to separate off the soluble acids (see below) and examine, in the first instance, the insoluble fatty acids.

The determination of the neutralisation number is carried out in exactly the same manner as described under the heading "Acid Value" (chap. vi. p. 277). As a rule, about 5 grms. of the substance should be taken; smaller quantities should not be employed, as otherwise the errors of the method have too great an influence on the result.

From the neutralisation number thus found, the mean molecular weight of the fatty acids can be calculated as follows:—Let M be the molecular weight expressed in grams; theory requires that M grms. be neutralised by 56·1 grams of potassium hydrate, KOH. Let n be the number of grams of potassium hydrate found by experiment to neutralise *one* gram of fatty acids, then we have the proportion

$$M : 56{\cdot}1 :: 1 : n \text{ ; hence, } M = \frac{56{\cdot}1}{n} \quad . \quad . \quad . \quad . \quad (1).$$

In order to find n, the number of c.c. of normal KOH found for 1 *grm. of fatty acid must be multiplied* by 0·0561. If that number be a, then, evidently, we have

$$n = a \times 0{\cdot}0561 \quad . \quad . \quad . \quad . \quad (2).$$

By substituting this expression in the above equation (1) we obtain

$$M = \frac{56{\cdot}1}{a \times 0{\cdot}0561} = \frac{1000}{a} \quad . \quad . \quad . \quad . \quad (3).$$

In the following table I give the theoretical molecular weights and calculated neutralisation values of pure fatty acids; they will serve as a guide in the proper interpretation of such numbers as are obtained in the practical examination of the mixed fatty acids of a given oil or fat.

Neutralisation Values of Fatty Acids

Acid.	Formula.	Molecular Weight.	Neutralisation Value.
Acetic	$C_2H_4O_2$	60	935·0
Butyric	$C_4H_8O_2$	88	637·5
Caproic	$C_6H_{12}O_2$	116	483·6
Caprylic	$C_8H_{16}O_2$	144	389·6
Capric	$C_{10}H_{20}O_2$	172	326·2
Lauric	$C_{12}H_{24}O_2$	200	280·5
Myristic	$C_{14}H_{28}O_2$	228	246·1
Palmitic	$C_{16}H_{32}O_2$	256	219·1
Daturic	$C_{17}H_{34}O_2$	270	207·7
Stearic	$C_{18}H_{36}O_2$	284	197·5
Oleic	$C_{18}H_{34}O_2$	282	198·9
Linolic	$C_{18}H_{32}O_2$	280	200·4
Linolenic	$C_{18}H_{30}O_2$	278	198·2
Ricinoleic	$C_{18}H_{34}O_3$	298	188·3
Arachidic	$C_{20}H_{40}O_2$	312	179·8
Erucic	$C_{22}H_{42}O_2$	338	166·0
Cerotic	$C_{26}H_{52}O_2$	396	141·7
Melissic	$C_{30}H_{60}O_2$	452	124·1
Hydroxystearic	$C_{18}H_{36}O_3$	300	187·0
Dihydroxystearic	$C_{18}H_{36}O_4$	316	177·6
Trihydroxystearic	$C_{18}H_{36}O_5$	332	169·0
Sativic	$C_{18}H_{36}O_6$	348	161·2
Linusic	$C_{18}H_{36}O_8$	380	147·6

I collate, in the following table, the neutralisation numbers and the calculated mean molecular weights of the mixed fatty acids of natural oils, fats, and waxes as obtained in the course of preparation described in Chapter III., p. 62.

Oil.	Class of Oil.	Group.	Neutralisation Number.	Mean Molec. Weight.
Perilla	Drying oils		197·7	283·7
Linseed			197	284·7
Tung oil			188·8	297·1
Stillingia			214·2	261·9
White acacia			200·1	280·4
Cedar nut			193·0	290·6
Echinops			192·3-192·9	291-292
Poppy seed			199	281·9
Sunflower			201·6	278·2
Yellow acacia			199	280·9
Clover, red; white	Semi-drying oils	Cotton seed oil group	283·2; 283·8	198·1; 197·6
Pumpkin seed			197	284·7
Watermelon			197·1	284·1
Maize [corn]			198·4	282·7
Kapok			191	293·7
Cotton seed			202-208	277·7-269·7
Sesamé			200·4	279·9
Croton			201	279·1
Garden cress		Rape oil group	193·2	290·3
Rape			185·0	303·2
Black mustard			187·1	300-299·8
White mustard			185·8	302-301·9
Radish seed			189·5	296
Jamba			173·9	322·6
Cherry kernel	Non-drying oils		189	296·8
Apricot kernel			194	289·1
Plum kernel			200·5	279·8
Peach kernel			200·9	279·2
Almond			204	275·0
Sanguinella			195·1	287·5
Arachis			201·6	278·2
Tea seed			195·0	286·0-287·6
Hazel nut			200·6	279·6
Olive			193	290·6
Coffee berry			175	320·5
Elderberry			204·8	273·9
Grape seed		*Castor oil group*	187·4	299·3
Castor			192·1	292·0
Herring	*Marine animal* oils	*Fish oils*	178·5	314·2
Stickleback			181·5	309·0
Cod liver		Liver oils	204-207	275·0-271·0
Tunny fish			177·0	316·9
Seal		Blubber oils	193·2	290·3
Egg	Terrestrial animal oils		194·9	287·8

Fat.	Class of Fat.	Group.	Neutralisation Number.	Mean Molec. Weight.
Palm	Vegetable fats		205·6	272·8
Akee			207·7	270·1
Macassar			191·6	292·7
Sawarri			205·6	272·8
Rambutan tallow			186·4	300·9
Cacao butter			190	295·2
Vegetable tallow			182-208	305·2-269·7
Kokum butter			198·9	282·0
Mocaya oil		Cocoa nut oil group	254	220·8
Palm nut oil			258-264	217·4-212·5
Cocoa nut oil			258-266	217·4-210·9
Myrtle wax			230·9	242·9
Japan wax			213·7	262·5
Blackcock	Animal fats	Drying fats	199·3	281·4
Hare			209·0	268·4
Rabbit (wild			209·5	267·7
Rabbit (tame)		Non-drying fats	218·1	257·2
Turkey			210·1	267·0
Fox			205·7	272·7
Horse			202·6	276·9
Horse marrow			210·8-217·6	266·1-257·8
Badger			193·7	289·6
Goose (domestic)			202·4	277·1
Goose (wild)			196·4	285·6
Chicken			200·8	279·3
Lard			201·8	278·0
Wild boar			203·6	275·5
Dog			199·2	281·6
Wild cat			203·8	275·2
Beef marrow			204·5	274·3
Bone			200	280·5
Beef tallow			197·2	284·4
Mutton tallow			210	267·1
Butter			210-220	267·1-255·0
Elk			201·4	278·5
Roebuck			200·5	279·8
Fallow buck			201·4	278·5
Chamois			206·5	271·6
Stag			201·3	278·6

2. Lactones—Anhydrides

It has been stated already that, as a rule, the amount of unsaponifiable matter may be neglected when the neutralisation number of the mixed fatty acids is determined. Hence, if the fatty acids, instead of being titrated with aqueous alkali in the cold, were boiled

with an excess of alcoholic potash (as is done when determining the saponification value of an oil), the number of milligrams of potassium hydrate so found for 1 grm. of fatty acids should be the same as the neutralisation value. In other words, the neutralisation value of the fatty acids should be identical with the saponification value of the fatty acids. In case, however, the fatty acids contain substances, *such as lactones, or anhydrides of the fatty acids, which do not combine* with aqueous alkali in the cold, but are only hydrolysed on boiling with alcoholic potash, then the saponification value of the fatty acids will be higher than the neutralisation number. *Tortelli* and *Pergami*[1] maintain that this holds good for all fatty acids, with the exception of stearic acid. They further state that the difference between the saponification number and the neutralisation number of the mixed fatty acids increases with the age of the sample. Their results are reproduced in the following table:—

[1] *L'Orosi*, 1901, 1.

Pure Fatty Acids.	I. Neutralisation Value.	II. Molecular Weight calculated from I.	III. Saponification Value.	IV. Molecular Weight calculated from III.	V. Difference, II.-IV.
Palmitic	202·7	276·5	218·7	256·4	20·1 (!!)
Stearic	198·7	282·3	198·9	282·0	0·3
Arachidic	163·9	342·3	170·1	329·8	12·5
Oleic, freshly prepared from olive oil	199·5	281·2	201·4	278·5	2·7
Oleic, 2 years old, from beef fat	191·0	293·8	202·8	276·6	17·2
Oleic, commercial, several years old	181·6	308·2	189·3	296·5	11·7
Mixed Fatty Acids from					
Linseed oil, fresh	194·6	288·2	201·8	277·9	10·3
,, ,, 3 years old	191·5	292·8	205·1	273·2	19·6
Sunflower oil, fresh	193·4	290·0	201·5	278·4	11·6
,, ,, 2 years old	194·5	287·6	199·6	281·0	7·6
Nut oil, fresh	200·2	279·7	202·8	276·3	3·4
Nut oil, same, kept in the dark 1 month	200·5	279·8	200·8	279·3	0·5
Nut oil, same, kept in the dark 2 months	196·0	286·2	208·5	269·0	17·2
Cotton seed oil, fresh	200·9	279·2	203·1	276·2	3·0
,, ,, 2½ years old	194·3	288·7	204·5	274·3	14·4
Ravison oil, fresh	176·8	317·3	183·2	306·2	11·1
,, ,, 2 years old	178·8	313·7	182·1	308·0	5·7
Rape oil, fresh	176·6	317·7	181·2	309·6	8·1
,, ,, 2 years old	178·3	314·6	182·5	307·4	7·2
,, ,, 5 years old	176·1	318·8	181·4	309·1	9·1
Castor oil, fresh	187·0	300·0	191·0	294·3	5·7
,, ,, 2½ years old	183·1	306·4	189·0	296·7	9·7
Cherry kernel oil	191·3	293·2	213·7	262·5	31·7
Apricot kernel oil, fresh	199·5	281·2	200·2	280·1	1·1
Apricot kernel oil, acids remained 1 month in the dark	196·0	286·2	199·1	281·7	4·5
Apricot kernel oil, acids remained 2 months in the dark	197·4	284·2	198·2	283·0	1·2
Apricot kernel oil, acids remained 5 months in the dark	187·0	300·0	200·0	280·5	19·5
Apricot kernel oil, 2 years old	196·8	285·0	200·0	280·5	4·5
Apricot kernel oil, same acids exposed to light 1 month	182·9	306·0	194·1	288·9	17·1
Almond oil, fresh	195·8	286·5	200·3	278·3	8·2
,, 2½ years old	196·0	286·2	202·2	277·5	8·7
Arachis oil, fresh	195·2	287·3	200·2	280·2	7·1
,, ,, 2½ years old	195·5	286·9	200·0	280·5	6·4
Hazelnut oil, fresh	197·6	283·8	199·7	280·9	2·9
Olive oil, 3 years old	194·5	288·4	200·9	279·1	9·3
Vegetable tallow, 3 years old	213·8	262·2	214·0	262·1	0·1
Vegetable tallow, acids exposed to light for 9 months	204·2	274·7	215·7	260·0	14·7
Lard, fresh	205·0	273·4	204·8	273·9	0·5
,, ,, 2½ years old	203·4	275·8	203·1	276·2	0·4
Beef tallow, fresh	205·7	272·7	209·9	267·2	5·5
,, ,, 2 years old	205·4	273·1	207·1	270·8	2·3

I have shown[1] that it would be premature to accept this as a general rule, since I have obtained in a number of cases figures contradicting *Tortelli* and *Pergami's* views. Whilst in some cases the numbers found agree with *Tortelli* and *Pergami's* statements, in other cases the differences are so small that they fall within the errors of the method. *In a number of cases even negative differences* were obtained, as will be seen from the following table, in which I collate the results ascertained in my laboratory :—

Neutralisation and Saponification Values of Mixed Fatty Acids (Lewkowitsch)

Acid from	I. Neutralisation Value.	II. Molecular Weight calculated from I.	III. Saponification Value.	IV. Molecular Weight calculated from III.	V. *Difference,* II.-IV.
Linseed oil	201·8	278·0	199·8	280·9	− 2·9
,, ,,	194·7	288·1	199·8	280·7	+ 7·4
,, ,,	195·2	287·4	199·0	281·9	+ 5·5
Tung oil	181·25	309·5	198·7	282·3	+27·2
Stillingia oil	206·3	271·9	210·5	266·5	+ 5·4
Nut oil	201·2	278·9	199·5	281·3	− 2·4
Safflower oil	200·3	280·1	199·7	280·9	− 0·7
Maize oil	197·1	284·6	199·8	280·7	+ 3·9
Cotton seed oil	197·4	284·1	204·2	274·7	+ 9·4
,, ,,	200·5	279·8	205·2	273·3	+ 6·5
,, ,,	201·9	277·8	205·1	273·5	+ 4·3
Rape oil	182·3	307·7	184·9	303·3	+ 4·4
Croton oil	197·3	284·3	203·3	275·9	+ 8·4
Castor oil	176·9	317·1	177·2	316·5	+ 0·6
,, ,,	175·7	319·3	177·8	315·5	+ 3·8
,, ,,	174·7	321·1	176·5	317·8	+ 3·3
Apricot oil	198·0	283·3	202·0	277·7	+ 5·6
,, ,, (California)	197·8	283·6	202·8	276·6	+ 7·0
,, *kernel*	194·0	289·1	200·7	279·5	+ 9·6
Peach kernel	196·8	285·0	205·0	273·6	+11·4
Almond (sweet)	196·4	285·6	201·7	278·1	+ 7·5
,, (Sicily)	198·8	282·1	202·2	277·4	+ 4·7
,, (Mazagan bitter)	196·8	285·0	203·1	276·2	+ 8·8
,, (small Indian)	195·8	286·5	200·7	279·5	+ 7·0
,, (Mogador bitter)	197·1	284·6	203·2	276·0	+ 8·6
,,	207·8	269·9	207·6	270·2	− 0·3
Olive oil	200·5	279·8	201·9	277·8	+ 2·0
,, ,,	200·9	279·2	200·9	279·2	0·0
Palm oil	206·2	272·0	206·9	271·1	+ 0·9
,, ,,	205·5	272·9	206·3	271·9	+ 1·0
Tallow seed oil	206·3	271·9	210·5	266·5	+ 5·4
Cocoa nut oil	271·6	206·5	271·0	207·0	− 0·5
,, ,,	271·5	206·6	270·6	207·3	− 0·7
Lard	196·0	236·2	205·1	273·5	+12·7
,,	196·2	285·9	204·5	274·3	+11·6
Margosa oil	194·1	289·0	198·9	282·0	+ 7·0
Pongam oil	192·5	291·4	195·8	286·5	+ 4·9
Oleic acid (iodine value 81·6)	201·2	278·8	201·4	278·5	+ 0·3

[1] Lewkowitsch, *Jahrbuch der Chemie*, xi. (1901), 359.

The difference between the saponification value and neutralisation value may be due to the formation of anhydrides of the fatty acids themselves on heating; in many cases it would point to the presence of inner anhydrides or lactones, the occurrence of which in fats and waxes has first been demonstrated by *Lewkowitsch*.[1] Thus wool wax fatty acids are easily converted on heating to 100° C. to some extent into inner anhydrides.

Hydroxylated fatty acids especially are likely to suffer dehydration with the formation of inner anhydrides. Thus the fatty acids of castor oil readily form inner anhydrides or polymerisation products; indeed it has been shown that the fatty acids of castor oil become polymerised even on prolonged keeping at the ordinary temperature, forming polyricinoleic acids (see chap. iii. p. 117). In the case of such polymerised ricinoleic acids a large difference between saponification value and neutralisation value will be found.[2] Another example of this kind is furnished by stearolactone, the inner anhydride of γ-hydroxystearic acid (see chap. iii.).

The lactones or anhydrides may be determined either volumetrically or gravimetrically.

(*a*) *Volumetric Determination of Lactones* (*Anhydrides*)

Five grams of the sample are weighed off, dissolved in neutralised alcohol, and titrated with aqueous alkali in the cold. It should be noted that the final solution must contain at least 50 per cent alcohol, as otherwise hydrolysis of the soap solution will set in, which must lead to erroneous results. Thus the neutralisation value of the sample is found. In another experiment 1·5 to 2·0 grms. are boiled with alcoholic potash in exactly the same manner, as described under "Saponification Value" (see chap. vi.) and titrated. Thus the saponification value is found.

The difference between the saponification value and the neutralisation value will be a measure of the lactones present. If the chemical composition of the lactone be known, its quantity can be calculated as shown by the following example:—

The saponification value of a mixture of fatty acids and stearolactone was found = 194·3, and its neutralisation number = 153·9. The difference, 194·3 − 153·9 = 40·4, corresponds to the amount of stearolactone present. Since the saponification value of stearolactone is 198·9, as calculated from:—

$$282 : 56{\cdot}1 = 1 : x\,; \quad x = 198{\cdot}9,$$

the percentage of stearolactone is found from the following proportion:—

$$198{\cdot}9 : 100 : : 40{\cdot}6 : x\,; \quad x = 20{\cdot}3 \text{ per cent.}$$

[1] *Proceed. Chem. Soc.* 1889, 69; *Journ. Soc. Chem. Ind.* 1890, 844; 1892, 39; 1896, 14.

[2] Cp. Lewkowitsch, *Journ. Soc. Chem. Ind.* 1893, 67.

Since the nature of the lactones (or anhydrides) present in a sample submitted to an analyst will but rarely be known, it will be found preferable to isolate the lactone and determine it quantitatively, as described in the following process, which admits at the same time of the volumetric determination of the free fatty acids.

(b) Gravimetric Determination of Lactones (Anhydrides)

Five grams or any other larger convenient quantity of the sample are dissolved in neutralised alcohol, and titrated with aqueous caustic potash in exactly the same manner as described above for the determination of the neutralisation value, the lactone or anhydride remaining unaffected as long as free fatty acid is present. The soap solution is then shaken out with ether or petroleum ether, as described under "Unsaponifiable Matter" (chap. vi. p. 293), care being taken not to dilute the soap solution so far as to cause dissociation of the soap (whereby acid soaps may pass into the ethereal solution). The ethereal solution is then filtered off, the ether evaporated off, and the residue weighed. The residue must be free from ash, and of course its neutralisation value must be *nil.*

If a further examination of the isolated lactone (or anhydride) be desired, its saponification value, iodine value, etc., may be determined.

3. Volatile Fatty Acids—Soluble Fatty Acids

If the saponification value of an oil or fat be found to lie considerably above 200, and consequently its *Reichert-Meissl* value be found to exceed 5, then the presence of volatile (soluble) fatty acids is proven. Since in the *Reichert* test a portion only of the volatile fatty acids is obtained, the further examination of the distillate and the isolation of the volatile fatty acids contained therein will not furnish complete information (see chap. xii.) as to the total volatile acids.

A measure of the total amount of volatile acids can, however, be obtained by the following differential method.[1] Saponify 4 to 5 grms. of the sample, weighed off accurately, with 60 c.c. of standardised (half-normal) alcoholic potash. The amount of potassium hydrate required to combine with the total fatty acids is then determined by titrating back the excess of caustic potash with half-normal hydrochloric acid, exactly as described under the heading "Saponification Value." Thus the saponification value of the sample is found. Next the alcohol is evaporated off, the soap dissolved in water and decomposed with hydrochloric acid. The liberated fatty acids are then washed on a filter with hot water, as described under "Hehner Value," to remove the soluble fatty acids. The insoluble fatty acids are then dissolved in neutralised alcohol and their neutralisation value determined by titration with half-normal caustic potash. By sub-

[1] Cp. Bondzyński and Rufi, *Journ. Soc. Chem. Ind.* 1890, 44.

tracting the neutralisation value thus found from the saponification value, the amount of potassium hydrate required for the neutralisation of the volatile (soluble) fatty acids will be obtained.

Example.—For the saponification of 5 grms. of a sample of butter fat 1130 mgrms. of KOH were used, and for the neutralisation of the insoluble fatty acids 920 mgrms. were required. The difference of 1130 - 920 = 210 corresponds to the alkali required for the soluble fatty acids in 5 grms. of butter fat. Hence, 42 mgrms. of KOH have been used per gram of butter fat.

If the mean molecular weight of the volatile (or soluble) fatty acids be known, their absolute quantity may be determined (cp. chap. xi. p. 406).

Another method, also furnishing a measure of the soluble acids, is *Morse* and *Burton's*;[1] it is based on the fact that the ratio between the quantities of alkali requisite for the neutralisation of the soluble fatty acids on the one hand, and of the insoluble fatty acids on the other, *is constant for any given fat.*

These relative quantities are given in the following table:—

Kind of Fat.	Per cent KOH required for	
	Insoluble Acids.	Soluble Acids.
Butter fat	86·57	13·17
Cocoa nut oil, not washed	91·85	8·17
„ „ washed with hot water	92·43	7·42
„ „ „ „ dilute soda	92·33	7·45
Cotton seed oil	92·05	7·76
Lard	95·96	3·82
Beef tallow	96·72	3·40
Oleomargarine	95·40	4·57

The following four standard solutions are required:—

1. Hydrochloric acid, 1 c.c. of which is equivalent to 20 mgrms. KOH.

2. Hydrochloric acid, 1 c.c. of which is equivalent to 2 mgrms. KOH.

3. Alcoholic potash (prepared with 95 per cent alcohol) approximately corresponding to acid No. 1. The strength of the potash solution must be determined accurately by titrating with the acid.

4. Alcoholic potash, corresponding to acid No. 2.

The analysis is carried out as follows:—

Place from 1 to 2 grms. of the dry and filtered fat—the exact quantity need not be known—in an Erlenmeyer flask of 250 c.c. capacity, and saponify with that amount of the strong potash solution which exactly equals 40 c.c. of the strong standard hydrochloric acid. Then add phenolphthalein, and titrate back the excess of alkali

[1] *Journ. Soc. Chem. Ind.* 1888, 697.

by the standard hydrochloric acid. This corresponds to the *saponification value.* Evaporate off the alcohol on the water-bath, and exactly liberate the fatty acids by adding just enough of the weaker standard acid; this quantity is, of course, the difference between 40 c.c. and the number of c.c. used for neutralising the excess of alkali after saponification. Next fit the flask with a condensing arrangement, consisting of a glass tube about 400 mm. long and 5 mm. in diameter, having its upper end bent downwards, and attached to a small U-tube containing water. This is designed to prevent the escape of volatile acids during the heating of the flask, which is continued until its contents become clear. Then filter the solution, to which is added the liquid from the U-tube, through thick paper, well wetted, and wash the insoluble fatty acids until the filtrate measures 1000 c.c. Next dissolve the insoluble acids in 50 per cent alcohol, and titrate with the strong potash solution; finally titrate the soluble acids with the weak potash solution.

The ratio only between the two amounts of alkali being required, it is neither necessary to weigh the fat nor to know the absolute strength of the standard alkalis.

The soluble acids are not necessarily identical with the volatile acids, although this is the case with the majority of oils and fats. But since a soluble dibasic acid has been discovered in Japan wax, due care must be exercised. If the total amount of the volatile acids only are required, they are best obtained in substance by a method similar to the one proposed by *Lewkowitsch* for the determination of the acetyl value. It consists in distilling off the total amount of volatile fatty acids exactly as described for the determination of the acetic acid in the acetyl distillation process. This method differs, of course, from the *Reichert* process in that the total amount of volatile fatty acids are driven off. Six to seven hundred c.c. are distilled off and the distillate is titrated with decinormal potash, using phenolphthalein as an indicator, and the number thus found calculated to 1 grm. of oil or fat. A few numbers have been ascertained by the "Filtration Process."

The following table contains the total volatile acids furnished by a number of commercial oils and fats[1]:—

[1] Lewkowitsch, *Analyst*, 1899, 319.

Volatile Acids in Commercial Oils and Fats (Lewkowitsch)

Kind of Oil or Fat.	Total Volatile Fatty Acids per gram; in terms of Mgrms. KOH.	
	Distillation Process.	Filtration Process.
Linseed (2 samples)	0·8-2·9	
Maize	2·53	
Cotton seed (4 samples of different age)	0·1-6·28	
,,	0·99	1·0
,,	2·0	2·1
,,	0·1	
Rape	2·15	
Croton (2 samples)	21·08	
Castor (3 samples)	0·0	
Olive	2·54	
Japan fish	1·78	
Fish, containing coast cod oil, etc.	9·22	
Cod liver, kept some years in bottle	2·60	
,, *fresh*	3·60	
Skate liver	0·80	
Shark liver	2·95	
Seal	1·50	
Horses' foot	4·07	
"*Animal*" *oil*	3·73	
Palm, containing 23·8 per cent free fatty acids	2·34	
Sawarri	1·07	
Cacao butter	2·80	
Palm nut, containing 6·68 per cent free fatty acids	19·55	
,, [1] ,, 6·94 ,, ,, ,,	11·4	
,, [2]	14·6	
,, [3]	22·2	
,, [4]	19·89	20·38
Cocoa nut, containing 9·9 per cent free fatty acids	{ 42·74 } { 42·29 }	
,, [1] ,, 3·9 ,, ,, ,,	20·9	
,, [2]	21·9	
,, [3]	26·7	
,, [4]	26·59	
,, [2] *containing 13·25 per cent free fatty acids*	26·4	
,, [3]	28·2	30·0
,, [4]	30·4	
Japan wax (2 samples)	5·6-10·05	
Lard	6·6	
Beef marrow	2·40	
Bone fat, containing 42·6 per cent free fatty acids	4·22	
Tallow, South American	7·24	
,, home melt I.	1·3	
,, ,, II.	4·8	6·0
,, ,, III.	1·4	1·7
,, Premier Jus	0·58	
Butter fat I.	49·3	
,, containing 0·56 per cent free fatty acids II.	43·32	
,,	41·4	
,,	32·0	31·3
,, containing margarine	12·8	

It will be seen from the table that in the case of those oils which

in their fresh state have a very low Reichert value, the amount of volatile acids increases with age. This is especially exemplified by cotton seed oil, tallow, palm nut, and cocoa nut oils.

The absolute quantity of the volatile fatty acids can be found by evaporating down the neutralised solution containing the potash salts of the volatile fatty acids to a small bulk, and finally drying in an oven to constant weight. By deducting from the weight thus found the weight of K_2O calculated from the amount of potassium hydrate used for the neutralisation of the volatile fatty acids, the amount of anhydrides of the volatile fatty acids is obtained. From this the molecular weight of the volatile fatty acids can be calculated (cp. chap. xi.).

4. Separation of Saturated from Unsaturated Fatty Acids

The presence of unsaturated fatty acids is detected in the readiest manner by determining the iodine value of the mixed fatty acids; this method offers the additional advantage of furnishing a measure of the unsaturated fatty acids, much as the iodine value of the oils and fats affords a measure of the unsaturated glycerides.

If no definite iodine absorption be found, it is safe to conclude that unsaturated fatty acids are absent.

The mixed fatty acids as obtained from the natural oils, fats, and waxes will always have a definite iodine value. From it some preliminary information may be obtained by reference to the following table:—

Iodine Values of the Mixed Fatty Acids

Oil.	Class of Oil.	Group.	Iodine Value.
Linseed	Drying oils		179-209·8
Tung			144-159
Lallemantia			166
Stillingia			161·9
White acacia			160·7
Cedar nut			161·3
Garden rocket			157
Hemp seed			141
Walnut			150
Echinops			139·1-143·8
Poppy seed			139
Sunflower			124-134
Yellow acacia			131·7
Fir seed			121·5
Madia			120·7
Cameline	Semi-drying oils	Cotton seed oil group	136·8
Clover, red; white			126·2; 122·2
Soja bean			119

Iodine Values of the Mixed Fatty Acids—continued

Oil.	Class of Oil.	Group.	Iodine Value.
Water-melon	*Semi-drying oils*	Cotton seed oil group	122·7
Maize (corn)			119·5
Wheat			123·3
Beech nut			114
Kapok			108
Cotton seed			111-115
Sesamé			110·45
Brazil nut			108
Croton			111·5
Curcas (purging nut)			105·1
Garden cress		Rape oil group	111·4
Rape (colza)			99-103
Black mustard			109·6
White mustard			95·3
Radish seed			97·1
Jamba			96·1
Cherry kernel	Non-drying oils		109
Cherry laurel			112·1
Apricot kernel			103
Plum kernel			103 (?)
Peach kernel			94-101
Almond			93-96·5
Sanguinella			102·8
Arachis			96-103
Pistachio			88·9
Elderberry			93
Hazel nut			90·3
Olive			86-90
Coffee berry			89·5
Ungnadia			86·5
Paradise nut			72·3
Grape seed		Castor oil group	99
Castor			87-93
Cod liver	Marine animal oils	Liver oils	130·5-170
Whale		Blubber oils	131·2
Egg	Terrestrial animal oils		72·9
Neat's foot			61·9-63·3

[TABLE

Iodine Values of the Mixed Fatty Acids—continued

Fat	Class of Fat.	Group.	Iodine Value.
Chaulmoogra	Vegetable fats		86
Laurel			81·8
Mowrah seed			56·6
Shea butter			55·6-57·2
Palm			53·3
Vegetable tallow			30-39
Akee			58·4
Macassar			50-58
Sawarri			51·5
Mafura tallow			47·5
Mkányi			42·1
Rambutan tallow			41·0
Cacao butter			33-39
Maripa			12·15
Palm nut			12·0
Cocoa nut			8·4-9·3
Blackcock	Animal fats	Drying fats	120
Hare			93·3
Rabbit (*wild*)			101·1
Rabbit (*tame*)		Non-drying fats	64·4
Starling			79·4
Turkey			70·7
Fox			65·4
Horse			84-87
Horse marrow			71·8-72·2
Badger			73
Pine marten			53
Goose (domestic)			65·3
Goose (wild)			65·1
Chicken			64·6
Polecat			60·6
Human, adult			64
Lard			64
Fat from wild boar			81·2
Dog			50·15
Wild cat			58·8
Domestic cat			54·8
Beef marrow			55·5
Bone			55·7-57·4
Beef tallow			41·3
Mutton tallow			34·8
Butter			28-31
Elk			31·9
Roebuck			28·9
Fallow buck			28·2
Chamois			24·4
Stag			23·6
Sperm oil	Liquid waxes		83·2-85·6
Arctic sperm oil			82·7
Wool wax	Solid waxes	Animal wax	17

Since these iodine values refer to the mixed *insoluble* fatty acids as prepared by the method described in Chapter III., the numbers given in the foregoing table do not necessarily stand in strict correspondence to the iodine values of the natural oils, fats, and waxes from which they have been derived. For the influence which soluble fatty acids, or mono- and diglycerides, in the original substances exercise severally on the iodine values of the glycerides, disappear in the case of the mixed fatty acids.

This will be seen at a glance on referring to the table (chap. vi. p. 250), and comparing the iodine values of mono-, di-, and triglycerides with the corresponding iodine values of their fatty acids.

If *only one unsaturated acid* be admixed with the saturated acids, and the chemical composition of the unsaturated fatty acid be known, then it is possible to calculate from the iodine value the absolute quantity of the latter, with the assistance of the table (chap. vi. p. 250). Thus if a given mixture of fatty acids have the iodine value 45·035, and it be known that the mixed fatty acids consist of saturated fatty acids *with oleic acid in admixture only*, then the absolute quantity of oleic acid will be found from the proportion :—

$$90·07 : 100 : : 45·035 : x; \quad x = 50 \text{ per cent.}$$

Even if a mixture of two unsaturated fatty acids of known composition, say oleic acid and linolic acid, be present, the respective amounts of oleic and linolic acids can be found from the iodine value of the mixed fatty acids if the absolute quantity of the solid acids, and hence also of the unsaturated acids, be known.

Such information would be furnished by a method permitting the quantitative separation of the saturated acids from the unsaturated ones. The several methods proposed hitherto for this purpose will be described under (*a*), (*b*), and (*c*).

(*a*) *Separation based on the Different Solubility of Salts of Fatty Acids in Organic Solvents*

A process for the separation of the solid fatty acids from liquid acids was proposed first by *Varrentrapp*. It is based on the solubility of the lead salts of the liquid fatty acids (oleic, linolic, and linolenic) in ether, the lead salts of the solid fatty acids (stearic, palmitic, etc.) being practically insoluble in that menstruum, as will be seen from the following table :—

Lead Salt of	100 c.c. of Ether dissolve	Observer.
	Grms.	
Palmitic acid . . .	0·0184	Lidoff[1]
Stearic acid . . .	0·0148	,,
Mixed stearic and palmitic acids (iodine value = 0)	0·0150 (at 25° C.)	Twitchell[2]

[1] *Berichte*, 26 Ref. p. 97. [2] *Journ. Soc. Chem. Ind.* 1895, 515.

But the solubilities of the lead salts of the solid fatty acids in ether are much increased if the ether holds notable quantities of lead salts of oleic acid and less saturated acids in solution. Hence *Varrentrapp's* process does not yield strictly accurate results, inasmuch as small quantities of the solid acids pass into the ethereal solution, as was shown first by *Mulder*,[1] whilst lead salts of the fatty acids of drying oils remain partly undissolved. *Lewkowitsch*[2] has also shown that a complete separation of the liquid from the solid acids cannot be thus effected. Therefore *the separation by means of the lead salts must be looked upon as a fractional* separation.

It must further be borne in mind, that the method effects chiefly separation of *solid* from *liquid* acids, which is not tantamount to a separation of *saturated* from *unsaturated* fatty acids, since erucic acid, as also isooleic acid, being solid yet unsaturated acids, are sparingly soluble in cold ether. Yet very frequently unsaturated fatty acids are considered as coterminous with liquid acids.

Notwithstanding these drawbacks and restrictions, *Varrentrapp's method is at present the best method at our disposal. This method* has been modified by several observers. I omit the description of those modifications which yield somewhat erratic results or have proved inconvenient in practical work, such as *Oudeman's*,[3] *Kremel's*,[4] *Röse's*[5] proposed modifications. The reader must therefore be referred to the original papers (or to the second edition of this work, pp. 193 and 194). I describe somewhat fully a combination of *Muter* and *de Koningh's*[6] modification with *Lane's*[7] suggestion, amplified by such explanatory details in working the method as have been found useful in my laboratory.

For this test either the mixed fatty acids or the neutral glycerides may be employed. Three to four grams of the sample are saponified in the usual manner with 50 c.c. of approximately half-normal alcoholic potash in a 300 c.c. flask. Phenolphthalein is added, the solution slightly acidified with acetic acid, and finally titrated with alcoholic potash until neutral. The solution is then diluted with water to about 100 c.c. Next 30 c.c. of a 10 per cent lead acetate solution are diluted with 150 c.c. of water and brought to the boiling point. This solution is gradually run into the soap solution with constant shaking, so that the saturated lead soap is made to adhere to the side of the flask, when the solution becomes cold. The flask containing the lead soap is filled up to the top with hot water, and then allowed to cool. When the liquid has become clear it is poured off through a filter; as a rule, the solution is so clear that no solid particles will be found on the filter. Otherwise they must be brought back into the flask. The precipitate in the flask is washed thoroughly with boiling

[1] Mulder, *Chemie der austrocknenden Oele*, 1867, p. 44 (German translation).
[2] *Journ. Soc. Chem. Ind.* 1890, 845.
[3] *Journ. f. prakt. Chem.* 99, 407.
[4] *Pharm. Centralhalle*, 5, 337.
[5] *Journ. Soc. Chem. Ind.* 1887. 306.
[6] *The Analyst* 1889, 61.
[7] *Journ. Amer. Chem. Soc.* 1893, February.

water, using the precaution to cool the hot solutions before filtering, and causing the lead salts to adhere to the sides of the flask. The last traces of water may be removed by means of a roll of filter paper. It is not advisable to dry the lead salts, as in the case of drying oils they somewhat rapidly absorb oxygen from the air. Next 150 c.c. of ether are added to the lead salts, the flask is corked and shaken repeatedly, so that the lead salts may disintegrate. The flask is then attached to a reflux condenser and heated on a water-bath for some little time with frequent shaking. The lead salts of the liquid fatty acids dissolve readily in the hot ether, conjointly with some portions of the salts of the saturated acids. When the undissolved salts settle out at the bottom of the flask as a fine powder, the heating is interrupted. If all operations are conducted somewhat rapidly, and unnecessary exposure to the air is avoided, working in an atmosphere of hydrogen can be dispensed with. The ethereal solution is then allowed to cool down to the ordinary temperature and filtered through a plaited filter, kept covered with a watch-glass, into a separating funnel. The insoluble salts are brought on to the filter by washing the flask three or four times with ether, using 30 c.c. each time. The ethereal solution is then shaken with a mixture of one part of hydrochloric acid and four parts of water, so as to decompose the lead salts. The ether dissolves the free fatty acids as they form, and the undissolved lead chloride settles out at the bottom of the separating funnel. After separating into two layers, the acid liquid is drawn off and the ether-layer washed with small quantities of water until the wash water is free from acid. Finally the ether solution is filtered through a small plaited filter into an ordinary flask. In case the liquid fatty acids consist chiefly of oleic acid, the results will be accurate enough if the ether is evaporated off on the water-bath and the residue dried in a water oven. If, however, less unsaturated fatty acids than oleic acid are suspected, then the ethereal solution should be distilled off in a current of dry hydrogen or dry carbonic acid. The flask is then immersed up to the neck in warm water which is at last brought to boiling point. Thus the last traces of moisture are removed.

This *modus operandi* has been found preferable to the use of a *Muter* tube, which involves the making up of the ethereal solution of the liquid fatty acids to 250 c.c., and determining the acids in an aliquot portion, say 50 c.c., as the drawing off of the ethereal solution is very apt to lead to errors. If it be desired, in special cases, as for the subsequent determination of the iodine value of the liquid fatty acids, to avoid exposure to the atmosphere during the weighing out of a portion of the liquid acids, the ethereal solution of the liquid fatty acids may be made up to a definite volume, say 200 c.c. 50 c.c. are then taken out by means of a pipette, transferred into a stoppered bottle, and the ether evaporated in a current of hydrogen or carbonic acid. Then the iodine solution is introduced, and the absorption determined in the usual manner. In that case the weight of substance taken is best determined in *another*

quantity of 50 c.c.,[1] which is treated in the manner described above. It will thus be seen that simultaneously with the determination of the quantity of liquid fatty acids contained in the mixed fatty acids, the iodine value of the liquid fatty acids may be ascertained. In fact this is always done, as very valuable information as to the nature of the liquid fatty acids is obtained from their iodine values. In the case of drying oils it is imperative to drive off the ether in a current of hydrogen or carbonic anhydride, as will be gathered from the following numbers obtained in my laboratory by *J. A. Walker*:—

Oil.	Iodine Value of the Liquid Fatty Acids.	
	Ether distilled off without using an Indifferent Gas.	Ether distilled off in a current of Carbon Dioxide.
Linseed	204·7	209·8
Candle nut . . .	183·0	185·7

The lead salts of the solid acids may also be isolated and their weight determined. This will provide a check for the accuracy of the analysis, as the weights of the solid and liquid acids added together should give the original weight. Furthermore the iodine value of the solid acids will indicate how much of the liquid acids has remained undissolved.

To show that approximate accuracy only is reached by this method, I give in the following table some results obtained in my laboratory by *H. E. Clapham*:—

Substance.	Weight used. G.	Ether Volume.	Temperature at which Ether Solution was kept.	Liquid Fatty Acids. Per cent.	Solid Fatty Acids. Per cent.	Iodine Value of Acids.		Loss. Per cent.
						Liquid.	Solid.	
Cocoa nut	3·3821	200 c.c.	15°-18° C.	24·36[2]	...	37·35	...	...
oleine	3·3931	200 c.c.	15°-18° C.	24·76	...	35·40	...	...
Whale oil	3·2791	75 c.c.	44° F. = 6·7° C.	77·28	19·78	126·86[3]	21·35	2·94
,, ,,	3·3124	75 c.c.	44° F. = 6·7° C.	78·76	17·93	126·08	19·77	3·31

The results depend on the temperature to which the ethereal solution is cooled and also on the quantity of ether used, and on varying these two factors different results were obtained. Losses amounting to several per cents in the quantities found are not easily avoidable. From the second series of experiments the conclusion must

[1] Cp. v. Raumer, *Zeit. ang. Chemie*, 1897, 210, 247.
[2] If the soluble acids are not removed by washing, they will be found amongst the liquid acids.
[3] For the true iodine value, cp. p. 359.

be drawn that too little ether was used, but even on employing larger quantities it is not possible to obtain the solid acids free from unsaturated ones (cp. "Linseed Oil," chap. xiv.).

If larger quantities of ether be used, more of the lead salts of saturated acids pass into the ethereal solution.

In place of ether, other solvents have been proposed, such as petroleum ether boiling below 80° C. (by *Twitchell* [1]), and benzene (by *Farnsteiner* [2]).

Farnsteiner's method is based on the solubility of the lead salts of the liquid fatty acids in benzene at the ordinary temperature, whereas the lead salts of the solid fatty acids are practically insoluble at temperatures below 8° or 12° C. At a somewhat elevated temperature the latter salts certainly dissolve in benzene, but on cooling to 8° or 12° C. they separate out in a crystalline form admitting of their being readily filtered off. Thus it was found that 100 c.c. of benzene dissolved only 0·0032 grms. of the lead salts of the solid fatty acids from tallow. The solid acids, prepared by repeated crystallisation of the mixed fatty acids from alcohol, melted at 62°-64° C.

The lead salts are prepared from the oil as previously described, and then dissolved in warm benzene, using 50 c.c. of the solvent for about 1 grm. of oil. On cooling to the ordinary temperature a crystalline deposit separates; the solution is then kept for two hours at a temperature from 8°-12° C. The supernatant liquid is best syphoned off by means of a small thistle funnel, covered with a piece of fine calico (to retain the crystals), and bent twice at right angles so that it may be fitted into a suction bottle connected with a filter pump. (This is preferable to *Farnsteiner's* proposal to force the liquid out by means of air pressure.) The precipitate is washed with 10 c.c. of benzene at 10° C., and again dissolved in 25 c.c. of warm benzene, cooled as before, and the solution filtered off as described. This operation may be repeated a third time so that, per gram of oil, there are obtained about 120-130 c.c. of a solution containing the lead salts of the liquid fatty acids. The free fatty acids are obtained as described above.

If benzene free from thiophene be used, the method would offer this advantage for the determination of the iodine value of the unsaturated fatty acids, that the solvent need not be driven off. This would render this process more convenient than the one described above, provided the quantitative results were better than, or at least equal to, those detailed above. I have, however, calculated from the experiments described by *Farnsteiner*, after applying the proper corrections, that the losses amount in some cases from 5·8 per cent to 9·6 per cent, so that preference should be given to the lead-salt-ether method. Possibly better results would be obtained if test experiments were made with larger quantities than *Farnsteiner* employed, namely, from 0·5 to 1·0 grms. of mixed fatty acids.

[1] *Journ. Soc. Chem. Ind.* 1895, 515.
[2] *Ibid.* 1898, 804; *Zeits. Unters. Nahrgs. u. Genussm.* 1898, 390.

If it is merely a question of isolating the unsaturated fatty acids in order to determine their iodine value, or otherwise examine them, a process worked out by *Tortelli* and *Ruggeri*,[1] and combining the advantageous features of the foregoing methods should be employed. This method has been extensively used in my laboratory, and can be recommended as giving reliable results. Unfortunately the process does not lend itself to the quantitative determination of the liquid fatty acids. *Tortelli* and *Ruggeri* operate as follows:—20 grms. of the sample are saponified with 15 c.c. of a 50 per cent potash solution, and 45 c.c. of 95 per cent alcohol. The excess of potash is neutralised with acetic acid, phenolphthalein being used as an indicator. In a half-litre flask 300 c.c. of 7 per cent lead acetate solution are heated to the boil, and the soap solution is poured into it in a thin stream with constant agitation. The flask is immersed in cold water and is kept therein for about ten minutes, with constant agitation. When the supernatant liquid has become clear, it is poured off and the lead soap is washed three times with 200 c.c. of warm (not boiling) water. The soap is allowed to cool, and large drops of adhering water are taken off with filter-paper. 220 c.c. of ether are then poured into the flask, the mass is thoroughly agitated, and warmed in a water-bath for twenty minutes until the ether just slightly boils; during this time the flask is shaken continuously, so as to detach all the soap from the sides and bottom of the flask. The flask is then immersed in cold water of 8°-10° C., and kept therein for *two hours*. The liquid is next filtered through a plaited filter into a 200 c.c. flask having a narrow neck. This flask is filled completely with ether, then well corked and left immersed in running water for twelve hours. As a rule, some precipitate will have settled out. The ethereal solution is then poured through a filter into a separating funnel, and the soap decomposed with 150 c.c. of 20 per cent hydrochloric acid. After running off the precipitated lead chloride and the aqueous solution, the ether is again shaken with 100 c.c. of the same hydrochloric acid. The ethereal solution is then washed with 150 c.c. of water, and finally poured through a plaited filter into a flask of about 300 c.c. capacity. Next the ether is distilled off so far that 40 to 50 c.c. remain in the flask. This solution is poured into another flask of about 100 c.c. capacity, fitted with a good cork, and the flask immersed almost completely in a water-bath. A current of dry carbonic acid is then passed through the ethereal solution and the water-bath heated until the ether is driven off.

The iodine numbers of the unsaturated fatty acids so prepared are the highest found hitherto, and for that reason must be accepted as coming nearest the truth. But, as has been pointed out already, this method does not admit of the quantitative separation of the saturated from the unsaturated acids. Thus in the preparation of the liquid fatty acids of whale oil, the iodine value of which was found = 144·6, the undissolved lead salts yielded acids having as high an iodine value as 70·0.

[1] *L'Orosi*, 1900, April.

(b) *Separation by means of Sulphuric Acid*

Twitchell[1] proposed to separate the saturated fatty acids from the unsaturated ones by their behaviour to sulphuric acid. Whereas the saturated acids are not chemically attacked by concentrated sulphuric acid, oleic acid and the less saturated acids combine with concentrated sulphuric acid to form compounds (cp. chap. iii.). Although these compounds are completely insoluble in petroleum ether, whilst the unattacked saturated acids dissolve in this menstruum, a method of separation cannot be based on the difference in solubility, since the solubility of all fatty acids in concentrated sulphuric acid is greater than their solubility in petroleum ether. Better results were obtained by *Twitchell* when employing 85 per cent sulphuric acid, which still forms a chemical compound with oleic acid. I have, however, shown[2] that this method does not lead to quantitative results. It can, therefore, only be employed for qualitative purposes.

(c) *Separation by Means of the Lithium Salts*

From the solubilities of the lithium salts given in the following table (due to *Partheil* and *Ferié*[3]), it will be gathered that the solubility of lithium oleate in alcohol differs sufficiently from that of lithium palmitate and stearate, so that a method of separation can be based on this difference.

	100 c.c. Water dissolves at		100 c.c. Alcohol (spec. grav. 0·797) dissolves at	
	18° C.	25° C.	18° C.	25° C.
	Grms.	*Grms.*	*Grms.*	*Grms.*
Lithium laurate . .	0·158	0·176	0·418	0·4424
,, myristate .	0·0235	0·0234	0·184	0·22
,, palmitate .	0·011	0·018	0·0796	0·0955
,, stearate . .	0·01	0·012	0·041	0·0532
,, oleate . .	0·0674	0·132	0·9084	1·009

Indeed, *Partheil* and *Ferié* proposed to separate the saturated from the unsaturated acids by means of the lithium salts. They proceed as follows:—1 grm. of the sample is saponified with 15 c.c. of approximately half-normal alcoholic potash in the usual manner on the water-bath, and the soap dissolved in 100 c.c. of 50 per cent alcohol. The excess of alkali is then exactly neutralised with dilute acetic acid, using phenolphthalein as an indicator, and a 10 per cent solution of lithium acetate in 50 per cent alcohol is added, whereby the lithium salts of palmitic and stearic acids are precipitated.

The flask is then warmed on the water-bath to 60° C., whereby the precipitate passes into solution. On cooling, lithium stearate,

[1] *Journ. Soc. Chem. Ind.* 1897, 1002. [2] Lewkowitsch, *Analyst*, 1900, 64.
[3] *Archiv. d. Pharmacie*, 1903, 552.

lithium palmitate, and the bulk of lithium myristate (if myristic acid be present) separate out as a crystalline precipitate. The precipitate is filtered off and washed with 50 per cent alcohol. The filtrate contains lithium oleate, the lithium salts of the less saturated acids, together with a small portion of lithium myristate (if myristic acid be present), and also the lithium salt of lauric acid (in case any lauric acid be contained in the sample).

In order to separate off the saturated acids—myristic and lauric (if any)—the dissolved lithium salts must be converted into their lead salts. The saturated acids are then separated from the unsaturated ones by the method described under (*a*).

5. Determination of Saturated Fatty Acids

The saturated acids obtained on separating off the unsaturated acids by means of the lead-salt-ether method will but rarely be free from unsaturated acids. (A measure of the latter can be obtained by ascertaining the iodine absorption of the acids isolated from the insoluble lead salts.) Still, for many purposes it may be preferable to work with these "saturated" acids than with the original mixed acids.

Experiments made by the author with a view to remove the adhering unsaturated fatty acids by converting them into their iodochlorides and separating the latter by crystallisation from the saturated fatty acids, have hitherto not led to satisfactory results.

(*a*) *Determination of Arachidic Acid*

The approximate determination of arachidic acid (frequently required in the examination of olive oils suspected of adulteration with arachis oil) is carried out by *Renard's*[1] process. The crude arachidic acid so obtained contains lignoceric acid, and the accurate determination depends on observing carefully a number of details. The method will be fully described in Chapter XIV., under "Arachis Oil."

(*b*) *Determination of Stearic Acid*

On triturating the mixed fatty acids from a solid fat with dilute alcohol of specific gravity 0·911 in a mortar, the unsaturated fatty acids are almost completely dissolved, the palmitic acid is partially dissolved, whereas the stearic acid remains almost completely undissolved. In a practical experiment the mixed solid acids so obtained had an iodine value of 2-3 only.

Far better results are obtained by treating the mixed fatty acids of an oil or fat with an alcoholic solution of pure stearic acid saturated at 0° C. *Hehner* and *Mitchell*,[2] following on the lines of earlier experiments made by *David*,[3] have shown by a series of experiments,

[1] *Compt. rend.* 73, 1330. [2] *Analyst*, 1896, 321.
[3] *Compt. rend.* 86, 1416; *Journ. Chem. Soc.* 34, 1011.

carried out on pure stearic acid and on mixtures of stearic acid with (*a*) saturated acids lower than palmitic; (*b*) palmitic acid; (*c*) crude oleic acid; (*d*) mixed saturated and unsaturated fatty acids (as *e.g.* mixed lard fatty acids), that stearic acid is left undissolved and can be determined quantitatively with great accuracy.

The analysis is carried out as follows:—Prepare a solution of stearic acid by dissolving about 3 grms. of pure stearic acid in 1000 c.c. of warm (methylated) alcohol of specific gravity 0·8183 (containing 94·4 per cent of alcohol by volume) in a stoppered bottle. Immerse the flask up to the neck in ice-water (kept in an ice-chest well protected against radiation of heat), and allow to stand in the ice-water overnight. After twelve hours, syphon off the mother liquor—without removing the flask from the ice-water—by means of a small thistle funnel immersed in the alcoholic solution and covered over with a piece of fine calico (so as to retain the separated stearic acid crystals in the flask). The funnel is twice bent at right angles, and is best fitted into a suction bottle, so that the clear liquor can be drawn off by means of a filter pump.

0·5 grm. to 1 grm. of the mixed fatty acids under examination, if solid, or 5 grms. if liquid, are weighed accurately in a flask and dissolved in 100 c.c. of the above alcoholic stearic acid solution. The flask is placed in ice-water overnight, the mixture is agitated next morning while the flask is kept in the ice-water, and then allowed to stand for at least half an hour in the ice-water in order to promote crystallisation. The alcohol is then filtered off as described above, care being taken to draw off the solution as completely as possible. The residue in the flask is washed three times in succession with 10 c.c. of the alcoholic stearic acid solution, and cooled down to 0° C. The crystals adhering to the calico of the thistle funnel are then washed off with hot alcohol into the flask, the alcohol is evaporated off, and the residue dried at 100° C. and weighed. This residue is considered as pure stearic acid. It is advisable to take the melting point of the acid; it should not be much below 68·5° C.

As the walls of the flask and also the undissolved crystals retain a small quantity of the alcoholic stearic acid solution, a correction must be applied. *Hehner* and *Mitchell* found that in their case the correction was 0·005 grm., which was deducted from the total weight of the residue found.

I can thoroughly recommend this method as giving reliable results in ordinary cases, as those represented by the mixtures with which *Hehner* and *Mitchell* experimented. In confirmation I may point to the following numbers found in my laboratory:—

Stearic Acid in	Per cent.
Palm oil, bleached	0·71; 0·72
Palm oil, raw (Bassa)	0·53
Butter fat	0·49
Cocoa nut oil	0·99
Bone fat	2·94
Tallow, several samples	21-22

This method unfortunately breaks down in the case of Japan wax fatty acids. In a number of experiments carried out upon mixtures of these acids with pure stearic acid, the latter could only be recovered partially in some cases, whereas in other cases none at all was obtained. This appears to be due to the influence of Japanic acid.

(*c*) *Determination of Palmitic Acid*

A method for the direct determination of palmitic acid in admixture with other solid acids is not yet known, but if, as is frequently the case (candle material), a mixture of stearic and palmitic acids, only be given, then its content in palmitic acid can be ascertained by determining the amount of stearic acid as described in the preceding paragraph, and deducting the weight found from the weight experimented upon. If the mixed acids contain unsaturated acids, allowance must be made for them by determining the iodine value and calculating to oleic acid, which in most cases will be sufficiently accurate (see below). Less accurate numbers are found by calculating the proportions of the two acids from the mean molecular weight of the mixed acids, in the manner shown in Chapter XI. p. 408.

A method of separating palmitic acid from stearic acid, due to *Kreis* and *Hafner*, will be described in Chapter XII.

(*d*) *Determination of Myristic Acid*

It has been shown above that on treating the lithium salts of the mixed fatty acids with 50 per cent alcohol, the bulk of the myristic acid is obtained together with lithium palmitate and stearate as a precipitate, whereas a smaller quantity of myristic acid passes into the solution together with lithium laurate, lithium oleate, and lithium salts of the less saturated acids.

The bulk of the myristate precipitated together with the stearate and palmitate can be separated from the stearate and palmitate by dissolving the mixed salts in hot absolute alcohol and allowing to cool. According to *Partheil* and *Ferié*, only the stearate and palmitate separate on cooling, whereas the myristate remains in solution. On filtering the solution, the stearate and palmitate remain on the filter.

The myristic acid is recovered by evaporating off the alcohol, dissolving the salt that remains behind in water, liberating the fatty acids by means of a mineral acid, and weighing the myristic acid.

The remainder of the myristic acid is recovered, together with the lauric acid, if any be present, by the method described under (*e*).

(*e*) *Determination of Lauric Acid*

The lithium laurate is found in solution together with lithium oleate, lithium salts of the less saturated fatty acids, and that portion

of the lithium myristate which has been dissolved in the process described above, in p. 353. The dissolved lithium salts are converted into lead salts, and the saturated acids separated from the unsaturated ones by means of the lead-salt-ether method. The solid acids liberated from their lead salts consist of lauric acid, or of a mixture of lauric and myristic acids.

Partheil and *Ferié* propose to ascertain the respective weights of lauric and myristic acids by determining the mean molecular weights of the mixed fatty acids, and calculating therefrom in the manner shown in Chapter XI.

The methods described under (*c*), (*d*), and (*e*) were carried out by *Partheil* and *Ferié* with such small quantities that strictly quantitative results can hardly be expected. Pending further confirmation of the accuracy of these methods, it would be possible by combining all the methods described under 4 (*a*) with those given under 5 (*a*), (*b*), (*c*), (*d*), and (*e*) to separate off all the higher saturated acids from the oleic and less saturated acids by means of the lead-salt-ether method, and then to determine in the liberated saturated acids in the first instance *arachidic* acid by following *Renard's* process. The remaining fatty acids would then be converted into their lithium salts, and lithium laurate and a small portion of the myristate removed by 50 per cent alcohol. The bulk of the myristate would be separated from the palmitate and stearate by absolute alcohol, and the *stearic* acid in the mixture of the last two salts determined in a direct manner as described under (*a*). The *myristic* and *lauric* acids would be determined as described under (*d*) and (*e*). The *palmitic* acid could then be found by difference. It must, however, be clearly understood that this course of analysis is merely derived from theoretical considerations, and requires confirmation by further experiments.

6. Determination of Oleic Acid in the absence of other Unsaturated Fatty Acids

If the insoluble fatty acids contain no other unsaturated acids than oleic acid, then its quantity can be determined from the iodine value of the mixed fatty acids, as shown above, p. 347. If a mixture of oleic, palmitic, and stearic acids be given, then each component of the mixture can be determined quantitatively as follows: Determine first the iodine value of the mixed fatty acids. Let this be I; then we find from the proportion

$$90{\cdot}07 : 100 :: \mathrm{I} : x ; \quad x = \frac{100\ \mathrm{I}}{90{\cdot}07} = 1{\cdot}1102\ \mathrm{I},$$

the percentage of oleic acid. Next determine the proportion of stearic acid by the method described above. By deducting the sum of the percentages found for oleic acid and stearic acid respectively,

the proportion of palmitic acid is found. The calculation from the iodine value and the mean molecular weights, as illustrated by the example given in Chapter XI., would be less accurate.

Less accurate still is a method proposed by *David*;[1] it is based on the greater solubility of oleic acid in a mixture of alcohol and acetic acid as compared with the solubility of palmitic and stearic acids. This method has been described in the second edition of this work, p. 197.

7. Detection, Separation, and Approximate Determination of the Individual Liquid Fatty Acids—Oleic, Linolic, Linolenic

As a preliminary operation it is necessary to separate the liquid fatty acids from the solid acids by the lead-salt-ether method. I recommend the following *modus operandi*:—First the amount of liquid fatty acids is determined approximately in 3 to 4 grms. of the mixed fatty acids or of the original oil by the method described p. 348. Then, in a fresh experiment, a larger quantity of liquid fatty acids is prepared by *Tortelli* and *Ruggeri's* method.

The next step is to determine the iodine value of the isolated liquid acids, in order to gain a preliminary insight into their composition. This will be readily obtained by referring to the table given in Chapter VI. and consulting the following table, in which I have collated the iodine values of the liquid fatty acids derived from a number of commercial oils and fats:—

Iodine Values of Liquid Fatty Acids derived from

Oil.	Class of Oil.	Group.	Iodine Value.
Linseed	Drying oils		190-209·8
Tung			179·7
Candle nut			185·7
Stillingia			178·1
Cedar nut			184
Walnut			167
Safflower			159·6
Poppy seed			150
Niger seed			147·5
Sunflower			154·3
Cameline	Semi-drying oils	Cotton seed oil group	165·4
Soja bean			131
Maize (corn)			140-144
Cotton seed			147-151
Sesamé			129-139·9
Ravison		Rape oil group	124·2
Rape (colza)			121-125

[1] *Compt. rend.* 86, 1416.

Iodine Values of Liquid Fatty Acids derived from—continued

Oil or Fat.	Class of Oil or Fat.	Group.	Iodine Value.
Cherry kernel	Non-drying oils		124·7
Apricot kernel			111·5
Plum kernel			98·6
Peach kernel			101·9
Almond			101·7
Arachis			105-128
Tea seed			99·6-104·4[1]
Hazel nut			91·3-97·6
Olive			95·5-103·5
Castor		Castor oil group	106·9
Salmon	Marine animal oils	Fish oils	197·4
Cod liver		Liver oils	167·6
Whale		Blubber oils	144·7
Tallow oil	Terrestrial animal oils		92·2-92·7
Lard oil			
,, ,, (European)			95·2-96·2
,, ,, (American)			103-105
Macassar	Vegetable fats		103·2
Palm			94·6
Akee			82·4
Vegetable tallow			97·04
Cocoa nut		Cocoa nut oil group	18·6 (?)
,, olein			36·3
Lard (European)	Animal fats		92·1-97·0
,, (American)			90-113
Beef tallow			92·4
Mutton tallow			92·7

Wallenstein and *Finck*[2] proposed for the iodine value of the liquid fatty acids the term "inner" or "absolute iodine number" of the oil. As it appears undesirable to multiply the number of terms that require a definition, I shall adhere in this work to the denomination "iodine value of the liquid fatty acids."

(a) *Mixture of Oleic and Linolic (Tariric, Elæomargaric) Acids*

If the mixed liquid fatty acids contain only oleic and linolic acids, then their respective quantities in the mixed liquid fatty acids can be

[1] Calculated. [2] *Journ. Soc. Chem. Ind.* 1895, 78.

calculated, and by referring these quantities to the original mixed fatty acid, or even original oil or fat, the absolute quantity of oleic and linolic acids may be determined. This assumption may hold good in those cases where the absence of linolenic acid has been proved by one of the methods described below. Let x be the proportion of oleic acid and y the proportion of linolic (tariric, elæomargaric) acid, and I the iodine value of the mixed liquid fatty acids, then we have, since the theoretical iodine values of oleic and linolic acid are 90·07 and 181·42 respectively, the following two equations:—

$$x + y = 100,$$

$$\frac{90 \cdot 07x}{100} + \frac{181 \cdot 42y}{100} = \text{I}.$$

From these two equations x and y can be calculated, and, as mentioned already, the figures so obtained are referred to the total mixed fatty acids or the original oil or fat.

The calculation of the respective quantities of oleic and linolic acids from the determination of their neutralisation numbers or their mean molecular weights, would obviously lead in this case to unreliable results, since their respective molecular weights, 282 and 280, lie too near to each other (cp. chap. xi. p. 407).

(*b*) *Mixture of Oleic, Linolic, and Linolenic Acids*

The further examination of the liquid fatty acids is somewhat complicated. *Hazura's*[1] investigations suggest the following two methods: firstly, the detection and identification of the liquid fatty acids by means of their oxidation products; and secondly, the identification of the liquid fatty acids by means of their bromo-derivatives.

1. *Isolation of the Oxidation Products of the Liquid Fatty Acids*

This method is based on the oxidation of the liquid fatty acids with a dilute alkaline solution of potassium permanganate. *Hazura* and *Grüssner* stated, as the outcome of their own and *Saytzeff's* researches, the following general law:—All unsaturated fatty acids, when oxidised with potassium permanganate in alkaline solution, have as many hydroxylated groups added as there are unsaturated valencies in the molecule—yielding as oxidation products saturated hydroxylated acids containing the same number of carbon atoms. A list of the hydroxylated fatty acids obtained by this method has been given already in Chapter III. p. 121, where the individual hydroxylated acids have also been described. In the majority of cases the oxidation products of oleic, linolic, and the linolenic acids, viz. dihydroxystearic, sativic, and linusic and isolinusic acids, will have to be looked for.

The process is carried out in the following manner:—30 grms. of the liquid fatty acids are neutralised with 36 c.c. of caustic potash of 1·27 specific gravity. The resulting soap is dissolved in 2000 c.c. of

[1] *Monatshefte f. Chemie*, 1887, 147; 156; 260. 1888, 180; 190; 469; 478; 944; 947. 1889, 190.

water, and an equal volume of a $1\frac{1}{2}$ per cent solution of potassium permanganate allowed to run in a thin stream with constant stirring. The solution is allowed to stand for ten minutes, and a quantity of sulphurous acid solution added, with continuous agitation, sufficient to dissolve all the precipitated hydrated manganese peroxide, and to impart an acid reaction to the solution. *Dihydroxystearic* and *sativic* acids are precipitated (A), whereas *linusic* and *isolinusic* acids remain dissolved (B).

The precipitated acids (A) are washed first with a little ether in order to remove some of the original liquid acids that have escaped oxidation, and then exhausted with large quantities of ether at the ordinary temperature, 2000 c.c. of ether being used for every 20 grms. of the precipitate. The *ethereal solution*, containing dihydroxystearic acid, is evaporated down to 150 c.c., when, on cooling, crystals are obtained which after recrystallisation from alcohol can be identified by their habitus, their melting point, molecular weight, and acetyl value as *dihydroxystearic* acid. That portion which was found to be insoluble in the cold ether is boiled out repeatedly with large quantities of water. Each quantity is filtered off boiling hot and allowed to deposit crystals on cooling, which are examined separately. They can be identified by their melting points and crystalline forms as *sativic* acid. Any insoluble acid will be recognised as dihydroxystearic acid that was not dissolved by ether.

The acid filtrate (B) is neutralised with caustic potash, boiled down to one-twelfth or one-fourteenth of the original volume and acidulated with sulphuric acid. The precipitate, consisting of a brown flocculent mass, is dried in the air and treated with ether, which dissolves azelaic acid and other acid secondary products of oxidation. The insoluble portion is then crystallised first from alcohol and then from water. *Isolinusic* and *linusic* acids are recognised by means of their melting points and by observing characteristic needles on the one hand, and obtruncated rhombic plates on the other. To effect a separation of the two acids the substance is recrystallised from a moderate quantity of water, so as to separate the more soluble isolinusic acid from the less soluble linusic acid. By weighing the several acids thus obtained, the quantitative composition of the liquid acids may be estimated approximately.

A synopsis of the preceding operations is given in the following table :—

Hydroxy Acids

A. Precipitate.		B. Filtrate.	
a. Soluble in Ether.	*b.* Insoluble in Ether.	*a.* Easily Soluble in Water.	*b.* Sparingly Soluble in Water.
Dihydroxystearic acid.	Sativic acid	Isolinusic acid	Linusic acid

The following table, summarising some of the properties of the four acids, will assist in mapping out another method of separation by means of the barium salts :—

Acid.	Formula.	Melting Point. °C.	Solubility of the						
			Acids in					Barium Salts in	
			Water.		Alcohol.		Ether.	Water.	
			Cold.	Hot.	Cold.	Hot.		Cold.	Hot.
Dihydroxystearic	$C_{18}H_{34}O_2(OH)_2$	137	Insoluble	Insoluble	Sparingly soluble	Soluble	Sparingly soluble	Insoluble	Insoluble
Sativic	$C_{18}H_{32}O_2(OH)_4$	173	Insoluble	Sparingly soluble	Sparingly soluble	Soluble	Insoluble	Insoluble	Insoluble
Linusic	$C_{18}H_{30}O_2(OH)_6$	203–205	Sparingly soluble	Soluble	Sparingly soluble	Sparingly soluble	Insoluble	Sparingly soluble	Readily soluble
Isolinusic	$C_{18}H_{30}O_2(OH)_6$	173–175	Sparingly soluble	Readily soluble	Soluble	Soluble	Insoluble	Sparingly soluble	Readily soluble

In the case of cod liver oil fatty acids, *Heyerdahl* found that under the conditions described above oxidation proceeds too far, 2 grms. only of hydroxylated acids having been obtained from 50 grms. of crude acids. Good results, however, were obtained when the oxidation was carried out with a half-saturated solution at the temperature of the freezing point.

For the oxidation of the higher unsaturated fatty acids, such as erucic and brassidic acids, a large excess of caustic potash must be used.

The foregoing method can only be employed as a qualitative one, since oxidation proceeds beyond the stage of hydroxylated acids. It will, however, be found useful if it be desired to prove the presence of oleic acid by the isolation of dihydroxystearic acid. For the detection of linolic and linolenic acid, however, the following method will be found perferable.

2. *Isolation and Determination of the Bromoderivatives of the Liquid Fatty Acids*

Hazura's earlier researches on the bromoderivatives of the unsaturated fatty acids have been supplemented by *Hehner* and *Mitchell* and by *Farnsteiner*. Their methods are based on the different solubilities of the bromides in solvents. This will be best understood by examining the following table, in which I have collated our present knowledge of the various bromides of the unsaturated fatty acids:—

[TABLE

Bromoderivatives of Unsaturated Fatty Acids

Bromoderivative from	Name of Acid.	Formula.	Molecular Weight.	Melting Point.	Containing Bromine.	Solubility in					
				°C.	Per cent.	Alcohol.	Ether.	Chloroform.	Petroleum Ether.	Benzene.	Glacial Acetic Acid.
Oleic acid	Dibromostearic Oleic dibromide	$C_{18}H_{34}O_2Br_2$	442	Oil	36·18	Readily soluble	Readily soluble	Readily soluble	Readily soluble	Readily soluble	*Readily* soluble
Elaidic acid	Dibromoelaidic Elaidic dibromide	$C_{18}H_{34}O_2Br_2$	442	27	36·18						
Linolic acid	Tetrabromostearic Linolic tetrabromide	$C_{18}H_{32}O_2Br_4$	600	113-114	53·33	Easily soluble	Easily soluble	Easily soluble	*Sparingly soluble*	Easily soluble	Easily soluble
Tariric acid	Tariric tetrabromide	$C_{18}H_{32}O_2Br_4$	600	125	53·33						
Telfairic acid	Telfairic tetrabromide	$C_{18}H_{32}O_2Br_4$	600	57-58	53·33	Easily soluble					
Linolenic acid	Hexabromostearic	$C_{18}H_{30}O_2Br_6$	758	177	63·32	Very sparingly soluble	Very sparingly soluble	...	Almost insoluble	Soluble	Very sparingly soluble
	Linolenic hexabromide	...	...	180-181							
Therapic acid	*(Octobromo-heptadecylic?)*										
	Therapic octobromide	$C_{17}H_{26}O_2Br_8$	902	...	70·95	Almost insoluble	Almost insoluble	Almost insoluble	...	Almost insoluble	Almost insoluble
Hydroxy acid in Quince oil	...	$C_{18}H_{34}O_3Br_2$	458	108	34·91	...	...	...	Soluble		
Ricinoleic	Dibromoricinoleic Ricinoleic dibromide	$C_{18}H_{34}O_3Br_2$	458	Oil	34·91	Soluble	Easily soluble				
Ricinelaidic	Dibromoricinelaidic Ricinelaidic dibromide	$C_{18}H_{34}O_3Br_2$	458	Oil	34·91						

The bromination test can be applied to the original mixed fatty acids without it being required to separate the solid acids from the liquid acids. *Hehner* and *Mitchell*[1] mainly directed their attention to the hexabromide derivative, thus arriving at the detection and approximate determination of the amount of linolenic acids. Their method is the same as the one described above in the hexabromide test (cp. chap. vii.):—0·3 grms. of the fatty acid are dissolved in glacial acetic acid, and the solution is cooled in a corked flask to 5° C. The further treatment is identical with that described already. For the quantitative determination *Hehner* and *Mitchell* recommend to completely remove the dibromide, and then determine the proportion of bromine in the *crude* hexabromide, which would consist of a mixture of hexabromides and tetrabromide. Since a hexabromide contains theoretically 63·32 per cent of bromine, and a tetrabromide 53·33 per cent, the respective amounts of acids can be calculated from the following two equations:—

$$x + y = 100,$$

$$\frac{63{\cdot}3x}{100} + \frac{53{\cdot}3y}{100} = B.$$

in which x is the percentage of hexabromides, y the percentage of tetrabromide, and B the percentage of bromine respectively in the crude bromides.

The following table contains a number of determinations of hexabromides from mixed fatty acids, carried out in my laboratory by *Walker* and *Warburton*:—

Kind of Oil.	Yield of Hexabromide from Fatty Acids. Per cent.
Linseed (iodine value = 181)	29·06 ; 29·34
,, (iodine value = 184)	31·31 ; 30·44 ; 30·80
,, liquid acids (iodine value = 208)	34·9
Candle nut	11·53 ; 11·23 ; 12·63
Stillingia	25·78
Safflower	1·65 ; 0·65
Japan fish	23·04 ; 23·32
Deodorised fish	38·42 ; 39·27
Genuine cod liver	29·86 ; 30·36
Newfoundland cod	39·1 ; 37·76
Shark liver	12·68 ; 15·08
Seal	19·83 ; 19·93
Whale	12·38 ; 12·44
Sperm	2·05

Whereas *Hehner* and *Mitchell* chiefly confined themselves to the determination of the hexabromides, *Farnsteiner* happily supplemented our knowledge of the bromides by more closely studying the tetrabromide. As will be seen from the table (p. 364), the different solubilities of oleic dibromide and linolic tetrabromide suggest a method of separation. Oleic dibromide is readily soluble in petroleum ether of boiling

[1] *Analyst*, 1898, 313.

point 35°-67·5° C., whilst linolic tetrabromide dissolves in it with great difficulty and on boiling only, the bromide separating on cooling in very fine, long, lustrous needles. 100 c.c. of petroleum ether at 12° C. hold in solution 0·014 grm. to 0·021 grm. of linolic tetrabromide, and at lower temperatures less still. Experiments instituted with weighed quantities showed, however, that a smaller quantity than 4·5 per cent of linolic acid could not be separated from a mixture of linolic and oleic acids.

In the following table I collate the proportions of linolic acid found by *Farnsteiner*. Although the numbers are only approximately accurate, they will furnish very useful indications. In the case of cotton seed oil, the percentage of linolic acid has been confirmed by determinations made in the writer's laboratory.

Oil or Fat.	Contains Linolic Acid.	Remarks.
	Per cent.	
Cotton seed oil	18·5	
Sesamé oil	15·8-12·6	
Rape oil	...	Linolenic present
Mustard oil	4·5	4 per cent linolenic
Almond oil	5·97	
Arachis oil	6·0	
Olive oil	Small quantity	
Horse fat	9·9	
Lard (European)	Small quantity	Traces of linolenic present
Tallow	...	" " "
Butter fat[1]	...	" " "

I have suggested[2] to combine the various methods described above by separating, in the first instance, the saturated fatty acids from the liquid fatty acids. Then brominate the liquid fatty acids, and determine the amounts of hexabromides by weighing the bromides insoluble in ether; next evaporate off the ether and separate the tetrabromide from the dibromide by means of petroleum ether. Calculate the hexabromide to linolenic, and the tetrabromide to linolic acid, so that the oleic acid can be found by difference. As a check the oleic bromide may be weighed. From the table (p. 364) it will be seen that any octobromide, due to the presence of therapic acid (*Heyerdahl*), might be also determined approximately by boiling out the crude hexabromides with benzene, when the hexabromide would pass into solution, leaving the octobromide behind. It should, however, be added that the suggested combination of these methods has not yet been examined experimentally.

For the separation of oleic acid from other liquid fatty acids, *Farnsteiner* suggested a method based on the (comparative) insolubility of barium oleate in benzene, containing alcohol, at low temperatures,

[1] The cows yielding this specimen of butter fat having been fed a long time on cotton seed cake, the linolenic acid found may be due to cotton seed oil (cp. "Butter Fat," chap. xiv.).

[2] *Jahrbuch der Chemie*, 1898 (viii.), 402.

whereas the barium salts of the less saturated acids are readily dissolved. Since the saturated acids behave like oleic acid, it would have been possible to separate a mixture of saturated and liquid acids of different unsaturation into a mixture of solid acids and oleic acid on the one hand, and less saturated liquid acids on the other hand. *Lewkowitsch*,[1] however, has shown that this method is useless for quantitative purposes.

8. Hydroxylated Fatty Acids

It has been shown above (p. 122) that hydroxystearic acid and dihydroxystearic acid are sparingly soluble in cold petroleum ether. This behaviour to solvents would suggest a method of isolating any hydroxylated fatty acids present in the mixed fatty acids by treating the latter with petroleum ether. But experiments made by the writer have shown that a method of this kind does not lead to useful results. For the mixed fatty acids from castor oil behave very much like castor oil (chap. xiv.), that is, they dissolve in an *equal* volume of petroleum ether. A mixture of castor oil fatty acids with oleic acid, however, could not be separated by means of petroleum ether.

In case the nature of the hydroxylated fatty acid in a sample is known, a measure thereof in the mixed fatty acids may be obtained by determining the increase of weight of the mixed fatty acids on boiling with acetic anhydride by *Lewkowitsch's* method (p. 289). Let M be the molecular weight of the monohydroxy acid, and i the increase of weight of A grams of the mixed fatty acids, then the percentage of hydroxy acids y will be (cp. equation, p. 289).

$$y=\frac{100Mi}{A.42}.$$

In the case of the hydroxy acid containing n hydroxy groups, and consequently being able to assimilate n C_2H_2O groups, we shall find

$$y=\frac{100Mi}{A.n.42}.$$

This method will, however, only lead to useful results if the amount of hydroxylated acids present in the sample be large (as in the case of castor oil); otherwise the loss in weight caused through the formation of anhydrides of fatty acids may counterbalance any gain in weight.

It will therefore be preferable to determine the acetyl value of the mixed fatty acids freed from volatile acids in a direct manner by distilling off and determining the acetic acid obtained on saponifying the acetylated acids.

For practical purposes the following table may be consulted :—

[1] *Analyst*, 1900, 64. *Zeit. Unters. Nahrungs. u. Genussm.* 1901, 62.

Acid.	Formula.	Acetylated Acid.				Increase in Weight on Acetylating.
		Formula.	Molecular Weight.	Acetyl Value.	Saponification Value.	Per cent.
Hydroxystearic	$C_{18}H_{35}O_2(OH)$	$C_{18}H_{35}O_2(O.C_2H_3O)$	342	164·0	328·0	14·00
Dihydroxystearic	$C_{18}H_{34}O_2(OH)_2$	$C_{18}H_{34}O_2(O.C_2H_3O)_2$	400	280·5	420·75	26·58
Trihydroxystearic	$C_{18}H_{33}O_2(OH)_3$	$C_{18}H_{33}O_2(O.C_2H_3O)_3$	458	367·4	489·9	37·95
Tetrahydroxystearic (Sativic)	$C_{18}H_{32}O_2(OH)_4$	$C_{18}H_{32}O_2(O.C_2H_3O)_4$	516	434·8	543·6	48·27
Pentahydroxystearic	$C_{18}H_{31}O_2(OH)_5$	$C_{18}H_{31}O_2(O.C_2H_3O)_5$	574	488·7	586·4	57·69
Hexahydroxystearic (Linusic)	$C_{18}H_{30}O_2(OH)_6$	$C_{18}H_{30}O_2(O.C_2H_3O)_6$	632	532·5	621·3	66·31

9. "Oxidised" Fatty Acids

Under the term "oxidised" acids I comprise a class of fatty acids occurring in those oils and fats which have been treated with oxidising agents, such as in the process of blowing with air or oxygen. The change which some of the unsaturated acids undergo is not understood yet, but this much is certain, that through "blowing" or "oxidising" a certain proportion of acids are obtained which are *characterised by their insolubility in petroleum ether.*

Fahrion,[1] who first proposed a method for the determination of "oxidised" acids in boiled linseed oil, assumed them to be hydroxylated acids, on account of their insolubility in petroleum ether, and their apparent similarity on that account to hydroxylated fatty acids. The fact, however, that these fatty acids can be separated from the others by petroleum ether, whereas, as I have shown (p. 367), a mixture of castor oil fatty acids and oleic acid cannot be resolved into its constituents, proves that they form a special class of acids for which, pending an inquiry into their nature, I proposed the name "oxidised" acids.

The *oxidised acids are determined by the following process*:[1]—4 to 5 grms. of the sample are saponified in the usual manner with alcoholic potash; the alcohol is evaporated off, the soap dissolved in hot water, transferred to a separating funnel, and decomposed with hydrochloric acid. After cooling, the liquid is shaken with petroleum ether (boiling below 80° C.), and allowed to stand until it has separated completely into two clear layers. The insoluble oxidised fatty acids will be found to adhere to the sides of the funnel or form a sediment in the petroleum ether layer. The aqueous layer is drawn off, the *petroleum ether layer is poured off, if necessary through a filter*, and the oxidised acids washed with petroleum ether to remove adhering fatty acids. *In case the amount of oxidised fatty acids be large*, it is advisable to dissolve them in alkali, decompose the soap with

[1] *Zeit. f. ang. Chemie*, 1898, 782.

hydrochloric acid, and shake out again with petroleum ether in order to completely remove any occluded ordinary fatty acids. The oxidised acids are then dissolved in warm alcohol, the alcoholic solution is transferred to a tared basin, the alcohol evaporated off, and the residue dried until the weight remains constant. Thus the proportion of oxidised acids is found.

The writer has prepared in this manner the oxidised acids from a solidified linseed oil. These acids have the following characteristics :— neutralisation value, 168 ; saponification value, 199·2 ; apparent acetyl value, 130·2. Further information will be found under the headings of "Blown Oils" and "Boiled Oils." The following table[1] shows the manner in which the proportion of oxidised acids increases with the increase of oxidation :—

	Specific Gravity at 15·5° C.	Saponification Value.	Oxidised Acids. Per cent.
Oleic acid	0·8952	201·4	
Oleic acid, blown 2 hours at 120° C.	0·9098	204·9	0·62
,, ,, ,, 4 ,, 120° C.	0·9121	206·0	2·6
,, ,, ,, 6 ,, 120° C.	0·9123	208·3	3·5
,, ,, ,, 10 ,, 120° C.	0·9238	213·4	6·0

These oxidised acids exhibit considerable acetyl numbers, as has been pointed out already (chap. vi.).

Further information on "oxidised" acids will be given in Chapter XV. under the heading "Oxidised Oils."

Lewkowitsch[2] assumes the presence of another kind of acid, differing from the "oxidised" acids, in blown oils. Pending further investigation they were termed "**unknown**" acids.

[1] Cp. *Laboratory Companion to Fats and Oils Industries*, Macmillan and Co., 1902, p. 76.

[2] *Analyst*, 1899, 323. Cp. also *Analyst*, 1902, 139.

CHAPTER IX

EXAMINATION OF UNSAPONIFIABLE MATTER

THE unsaponifiable matter is necessarily isolated in substance in the course of its quantitative determination, and can therefore be further examined immediately.

In the case of natural oils and fats the quantity of unsaponifiable matter will, as a rule, be small, but in the case of waxes it will constitute a large proportion of the original substance, as pointed out already.

If the natural oils, fats, and waxes have been adulterated with such substances as paraffin wax, ceresin, mineral oils, neutral tar oils, and rosin oils, these substances will be obtained together with the unsaponifiable substances. Their detection and estimation will be considered briefly in this chapter.

The subject of this chapter naturally divides itself into two groups, A,—examination of those unsaponifiable substances which are naturally present; and B,—examination of the substances found under A together with foreign unsaponifiable substances that have been admixed with them.

A. EXAMINATION OF THE NATURALLY PRESENT *UNSAPONIFIABLE SUBSTANCES*

1. In Oils and Fats

If considerable quantities of unsaponifiable substances are present, they will be observed in the course of the process of saponification. The alcohols or hydrocarbons present will be found floating on the top of the neutralised alcoholic soap solution as an oily layer. Small quantities, however, will always remain in solution, or form an emulsion with the soap solution.

The unsaponifiable matter will contain chiefly (besides small quantities of colouring matters, resinous substances and albuminoid bodies) either cholesterol or phytosterol. The detection of cholesterol and phytosterol, or of a mixture of both, becomes of great importance whenever the question is placed before the analyst to decide whether a given sample is of vegetable or animal origin, or whether a mixture of vegetable or animal oils or fats is under examination.

How far this is affected by Gill and Tuft's statement that maize oil is characterised by sitosterol, must be decided by further investigations.

The colour reactions given above (chap. iii.) for cholesterol and phytosterol are not distinct enough to allow to discriminate between the two alcohols. Recourse must, therefore, be had to the following methods :—

(*a*) *Microscopic Examination* [1]

The unsaponifiable matter, after weighing, is dissolved in ether and poured into a small porcelain dish. The ether is allowed to evaporate off spontaneously, the mass is then dried on a water-bath,

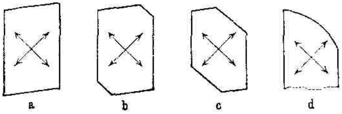


Fig. 38.—(*a*) Crystals of Cholesterol.

dissolved, after cooling, in the smallest possible quantity of absolute alcohol, and then allowed to crystallise. As a rule, well-defined crystals will be obtained, unless the amount of colouring matter and resinous substance present is too large. In those cases it will be advisable to dissolve the unsaponifiable matter in 95 per cent alcohol and remove the colouring matters by treating in the hot with charcoal, and filtering off the hot alcoholic solution. The filtrate is then evaporated to dryness, and again taken up with absolute alcohol. A few crystals are then taken out and examined carefully under the microscope. If either cholesterol or phytosterol alone are present, the crystalline forms characteristic of cholesterol or phytosterol will be found (Fig. 38). If, however, there be present a mixture of cholesterol and phytosterol, the information furnished by the microscopic examination becomes very uncertain, since mixed forms of cholesterol and phytosterol are obtained (Fig. 38 (*c*)), as has been stated by *Bömer*. In my own experience I did not obtain the mixed forms of crystals from artificial mixtures of cholesterol and phytosterol, but found that

[1] Bömer, *Zeits. Unters. Nahrgs. u. Genussm.* 1898, 544.

each constituent crystallised separately, the two different forms lying side by side in the mother liquor.[1] On crystallising rapidly, in most cases flocks separated, which showed distinct crystalline form; in case, however, crystals could be observed, they appear to simulate the crystalline form of phytosterol. On filtering off the first crop

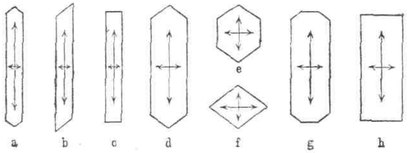


Fig. 38.—(b) Crystals of Phytosterol.

and allowing them to crystallise, better crystals are obtained, showing distinctly the individual cholesterol crystals, side by side with phytosterol crystals.

These observations are confirmed by *Zetsche*,[2] who published a number of drawings which I reproduce here (Figs. 39-49).

Therefore, the microscopic examination of the alcohols themselves

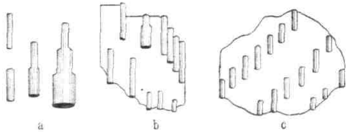


Fig. 38.—(c) Crystals from a mixture of Cholesterol and Phytosterol.

should only be looked upon as a preliminary test, not permitting a definite conclusion to be drawn as to the absence of phytosterol or cholesterol in animal and vegetable fats respectively. In order to arrive at decisive results, it becomes necessary to carry out the "phytosterol acetate test."

(b) *Phytosteryl Acetate Test* [3]

The alcoholic solution containing the crystals, see (*a*), is brought to dryness on a water-bath, and heated in a dish with 2 to 3 c.c. of acetic anhydride for a minute over a small flame

[1] *Journ. Soc. Chem. Ind.* 1899, 557. [2] *Pharm. Central-Halle*, 1898, No. 49.

[3] Bömer, *Zeits. Unters. Nahrgs. u. Genussm.* 1901, 1091; *Journ. Soc. Chem. Ind.* 1902, 192.

until it boils, the dish being covered with a watch-glass. The watch-glass is then removed, and the excess of acetic anhydride evaporated off on the water-bath. The contents of the dish are next heated with the smallest quantity of absolute alcohol, and in order to prevent *immediate solidification or crystallisation* a few c.c. of alcohol are added, and the mass allowed to crystallise. By spontaneous evaporation about one-half or one-third of the alcohol is removed whilst the

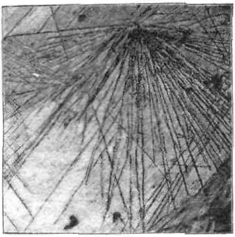


Fig. 39.—Crystals from Cholesterol (from ether).

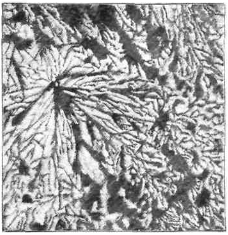


Fig. 40.—Crystals of Phytosterol (from ether).

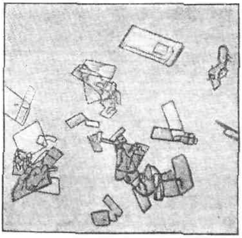


Fig. 41.—Crystals of Cholesterol (from alcohol ; on glass cover).

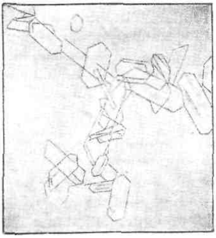


Fig. 42.—Crystals of Phytosterol (from alcohol ; on glass cover).

acetates crystallise out. The crystals are filtered off through a small filter, and washed with a little 95 per cent alcohol. The crystals are brought back into the dish, and dissolved in 5 to 10 c.c. of absolute alcohol, and again allowed to crystallise. These crystals are filtered off, and their melting point is determined. Since the cholesteryl acetate melts at 114·3°-114·8° C. (*corr.*), whereas crystals of phytosteryl acetate obtained from different oils and fats melted from 125·6° to 137° C. (corr.), the melting point of the second crop of crystals will give preliminarily the information whether

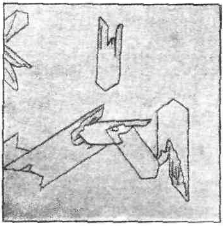


Fig. 43.—Crystals of Cholesterol containing 7 per cent Phytosterol (from alcohol; on glass cover).

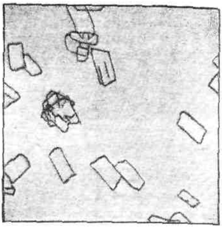


Fig. 44.—Crystals from Pure Lard (from alcohol; on glass cover).

Fig. 45.—Crystals from Pure Lard (from alcohol; taken out of mother liquor).

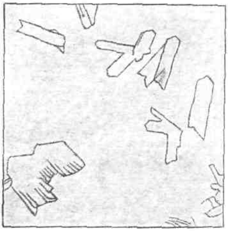


Fig. 46.—Crystals from Lard containing 5 per cent cotton seed oil (from alcohol; on glass cover).

Fig. 47.—Crystals from Lard containing *5 per cent cotton seed oil (from alcohol*; on glass cover).

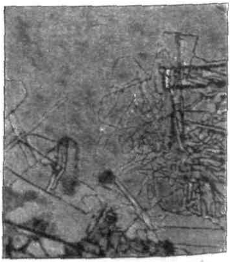


Fig. 48.—Crystals from Lard containing *5 per cent cotton seed oil* (from alcohol; taken out of mother liquor).

cholesterol only or phytosterol be present. Ultimate reliance should, however, not be placed on the melting point of the second crop of crystals, for in doubtful cases it is necessary to recrystallise the crystals three more times. If, *e.g.* the melting point of the fifth crop of crystals be found below 116°, then the absence of phytosterol can

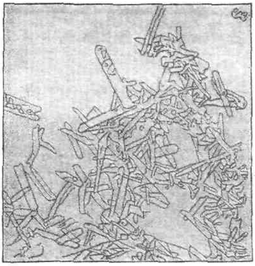


Fig. 49.—Crystals from Lard containing 10 per cent cotton seed oil (from alcohol; taken out of mother liquor).

be pronounced with certainty. If the first crop of crystals is deeply coloured by foreign substances (a not infrequent occurrence), it is advisable to remove the bulk of them by pressing the crystals between filter paper before the mass is further recrystallised. Further information will be given in Chapter XIV. under "Lard."

2. In Waxes

In the case of waxes, the large amount of alcohols will reveal itself by the fact that saponification is not readily effected, especially so in the case of wool wax. In these cases it is best to saponify with double normal alcoholic potash under pressure, or preferably with sodium alcoholate (cp. chap. ii.).

The solid unsaponifiable constituents obtained on saponifying waxes consist of a mixture of aliphatic alcohols—cetyl alcohol, ceryl alcohol, myricyl alcohol, etc., cholesterol, isocholesterol (notably in the case of wool wax), and small quantities of hydrocarbons.

Since the isolated unsaponifiable solid matter does not consist of one chemical individual only, ultimate analysis will not lead to any useful information. This will only be the case if, in the course of the examination, pure substances have been obtained.

The determination of the melting point will only furnish some little preliminary information, as will be seen from the following

table giving the melting points of those substances most likely to be met with :—

Unsaponifiable Substance.	Melting Point. °C.
Cetyl alcohol	50
Ceryl alcohol	79
Myricyl alcohol	85
Cholesterol	148·4-150·8
Isocholesterol	137-138
Phytosterol	138-143·8
Beeswax hydrocarbon $C_{27}H_{56}$	60·5
,, ,, $C_{31}H_{64}$	67
Paraffin wax	from 38 to 82
Ceresin	from 61 to 78

If a mixture of several of these substances be present, then the melting point becomes of still less importance, as small quantities of impurities depress the melting point considerably. Only in case a very high melting point has been obtained, conclusions may be drawn as to the presence of cholesterol, but it should be remembered that a mixture of cholesterol and isocholesterol melts below 100° C.

A measure of the proportion of alcohols in a mixture can be obtained by the following methods—

1. Weigh off accurately the mixed substances and boil in a flask with twice the weight of acetic anhydride under a reflux condenser. Pour the acetylated mass into 300 c.c. of boiling water to decompose the acetic anhydride, allow to cool, and then filter off the separated mass on a weighed filter (cp. chap. vi. Di- and Monoglycerides), wash until the wash waters are no longer acid, and dry to constant weight. From the increase in weight, preliminary information may be gathered as to the proportion of alcohols present, on consulting the following table (p. 379).

2. On observing the behaviour of the unsaponifiable substance to acetic anhydride, some important information can be gathered as to the composition of the unsaponifiable matter. The following three cases may present themselves, and one or other of the three events will happen :—

(*a*) The unsaponifiable matter is completely dissolved in acetic anhydride, and no separation takes place on cooling. This points to the presence of *aliphatic* alcohols.

(*b*) The unsaponifiable matter dissolves completely on boiling; on cooling, a magma of crystals separates out. This indicates the presence of *cholesterol* or *phytosterol*, or of some higher aliphatic alcohols, or a mixture of these substances.

(*c*) The solution is not homogeneous, a clear oily layer floats on the top of the hot acetic anhydride. This indicates the presence of notable quantities of hydrocarbons (paraffin wax, ceresin, etc.); at the same time there may be present alcohols, as described under (*a*) and (*b*). The presence of cholesterol would be recognised as under (*b*).

If the lower layer be clear on cooling, then the possibility that alcohols of the aliphatic series are present must be taken into account.

On this different behaviour to acetic anhydride, a rough separation of the hydrocarbons from the alcohols can be based by proceeding in the following manner, which I have frequently employed with advantage. The hot acetylated mass is transferred to a small separating funnel of thin-walled glass, as little acetic anhydride as possible being used to rinse the flask, and the separating funnel is carefully warmed, so that all the alcohols remain in solution and two distinct layers are obtained. If too much acetic anhydride be used, some hydrocarbons pass into solution.[1] The clear lower layer is drawn off and examined for alcohols, as described below, and the top layer washed with a small quantity of acetic anhydride in the hot. The hydrocarbons are then allowed to cool, washed with boiling water on to a filter, and weighed. They may then be further examined by determining their melting point (and iodine absorption, if deemed necessary). If no oily layer has been observed on the top of the acetic anhydride, or in presence of such, after it has been separated off, the hot acetic anhydride solution is run into boiling water, and the separated acetates of cholesterol and aliphatic alcohols washed on a filter until the wash waters are no longer acid.

By determining the saponification values of the acetates on the filter in the manner described under the heading "Saponification Value," and comparing the numbers so found with those recorded in the table given below, some further information will be gathered as to the composition of the original alcohols.

If a mixture of aliphatic alcohols with cholesterol or phytosterol be suspected, it will be useful to remember that the acetates of cholesterol and phytosterol require larger quantities of hot 95 per cent alcohol to dissolve completely than aliphatic alcohols, the latter dissolving easily.

If the quantity of the acetates at disposal permit, the several acetates may be approximately resolved into their constituents by fractional crystallisation from alcohol, and the saponification and iodine values of the several fractions determined.

Complete separation, however, cannot be effected, as has been shown by *Lewkowitsch*.[2] In a mixture prepared from weighed quantities of cholesterol and cetyl alcohol he obtained in two experiments 60 and 69 per cent of the theoretical quantities of pure cholesteryl acetate in the first crop of crystals, whilst the second crop of crystals—9 per cent—contained notable quantities of cetyl acetate. Again, on boiling the wool wax alcohols [consisting of cholesterol, isocholesterol, ceryl alcohol, and other unknown alcohols] with acetic anhydride, and trying to separate the acetates by crystallisation from alcohol, *Lewkowitsch* isolated ceryl acetate in a crystalline state, whilst the acetates of the cholesterols formed with

[1] Cp. Marcusson, *Mitth. König. Techn. Vers.-Anst.* 1900, 261.
[2] *Journ. Soc. Chem. Ind.* 1892, 143.

the acetates of the unknown alcohols oily substances from which no *crystals could be obtained.*

On titrating back the excess of caustic potash used on saponifying the several acetates, the alcohols separate out. They are precipitated completely by addition of water, and can be recovered quantitatively for further examination. It will be useful to determine the melting point, and the iodine value of the isolated alcohols, and apply the colour tests for cholesterol and isocholesterol.

Cholesterol and isocholesterol, if present, may be partially separated from each other by means of their benzoates. These are prepared by heating the alcohols with 4 parts of benzoic anhydride [1] in a sealed tube to 200° C. for thirty hours (p. 143). The product is boiled out repeatedly with alcohol, in order to remove any adhering aliphatic alcohols.

The mixed benzoates are then dissolved in ether and allowed to crystallise. The cholesteryl benzoate crystallises in hard rectangular plates, whereas the isocholesteryl benzoate is obtained as a light crystalline powder, which can be roughly separated from the former by decantation and elutriation. *Cholesteryl benzoate melts at 150°-151° C.*, isocholesteryl benzoate at 190°-191° C. As a confirmatory test, *the benzoates should be saponified with alcoholic potash, and the* cholesterol and isocholesterol precipitated by diluting with water. The separated alcohols may be further identified by their optical rotations and melting points.[2]

In the following table I give a synopsis of those characteristics that will prove of assistance in the examination of the solid unsaponifiable substances :—

[1] Schulze, *Berichte*, 5. 1076; 6. 251, 571; *Journ. prakt. Chemie*, 115. 163.
[2] Lewkowitsch, *Journ. Soc. Chem. Ind.* 1892, 142.

Some Unsaponifiable Substances and their Characteristics

	Formula.	Melting Point. °C	Iodine Absorption.	Acetates.		Increase in Weight on Boiling with Acetic Anhydride.[1]
				Saponification Value.	Melting Point. °C.	Per cent.
Cetyl alcohol . .	$C_{16}H_{34}O$	50	0	197·5	22-23	17·2
Octodecyl alcohol .	$C_{18}H_{38}O$	59	0	180·0	31	15·5
Ceryl alcohol . .	$C_{27}H_{56}O$	*79*	0	128·1	*65*	*10·6*
Myricyl alcohol .	$C_{30}H_{62}O$	85	0	116·7	70	9·6
Cholesterol . .	$C_{26}H_{44}O$	148·5	68·3	135·5	114	11·3
Isocholesterol . .	$C_{26}H_{44}O$	137-138	68·3	135·5	...	11·3
Phytosterol . .	$C_{26}H_{44}O$	137-138	68·3	135·5	125·6-137	11·3
Sitosterol . .	$C_{27}H_{44}O + H_2O$	137·5	...	...	127·5	
Mixed alcohols from sperm oil	?	25·5-27·5	64·6-65·8[2]	161-190		
Mixed alcohols from neutral wool fat	?	...	36	160·9		
Mixed alcohols from crude wool fat	?	...	...	150·6[3]		
Mixed alcohols from beeswax	?	75-76	...	99-103	...	6·5-7·7
Mixed alcohols from carnaüba wax	?	85	...	123	...	10·21
Paraffin wax, Ceresin	...	*38-82*	*3·9-4·0*[4]	...	...	*0*

Reliable methods of separating aliphatic alcohols from cholesterols are not yet available. Two methods, however, have been proposed *which may lead to satisfactory results when fully worked out.*

Lewkowitsch[5] bases a method of separation on the conversion of aliphatic alcohols into fatty acids by heating with soda-lime or potash-lime, cholesterols remaining practically unchanged. Crucial experiments carried out with sperm oil alcohols and with cholesterol showed that on heating the former with soda-lime the bulk of the alcohols were converted into fatty acids, only 4 to 6 per cent of unchanged alcohols being recovered; whereas on treating cholesterol in the same manner 93 per cent of unchanged alcohol were recovered, traces only of fatty acids having been formed.

Cochenhausen[6] proposes to heat the mixture of aliphatic alcohols and cholesterols with conc. sulphuric acid, when the aliphatic alcohols yield alkyl sulphates, whereas the cholesterols are converted into hydrocarbons—"cholesterones." The alkyl sulphates can be isolated by means of their sodium salts, and the original alcohol may be

[1] Lewkowitsch, *Journ. Soc. Chem. Ind.* 1896, 14.

[2] The iodine values of the fractions into which the mixed alcohols were resolved (*Journ. Soc. Chem. Ind.* 1892, 135) were the following:—1, 46·48; 2, 63·3; 3, 69·8; 4, 81·8; 5, 84·9.

[3] Iodine absorption = 44·03 per cent.

[4] Determined in the writer's laboratory.

[5] *Journ. Soc Chem. Ind.* 1892, 13; 1896, 14.

[6] *Ibid.* 1897, 447.

recovered therefrom by decomposition with boiling hydrochloric acid. Experiments, however, made on wool wax alcohols have not yet led to satisfactory results.

If a mixture of aliphatic alcohols only be given, the method proposed first by *C. Hell* [1] and employed later by *Buisine* for the examination of beeswax, may give some useful indications. The process is based on the fact that, on heating an aliphatic alcohol with soda-lime, one molecule of the corresponding fatty acid is formed, with evolution of two molecules of hydrogen, as explained by the equation—

$$\underset{\text{Cetyl alcohol.}}{C_{16}H_{33}\cdot OH} + NaOH = \underset{\text{Sodium palmitate.}}{C_{16}H_{31}O_2Na} + 2H_2.$$

It is therefore possible to infer from the volume of liberated gas, the amount of alcohol originally present. According to *Hell*, the substance, intimately mixed with soda-lime is introduced into the tube *i* (Fig. 50), and the mixture covered with soda-lime. In order to reduce the volume of air to the smallest possible amount, the sealed tube *k* is placed inside tube *i*. The latter is closed by a perforated india-rubber stopper *p* provided with tube *r*, which connects *i* with a *Hofmann* gas burette, filled completely with mercury, and closed at the top by means of the three-way tap *h*. The tube *i* is then immersed in an air-bath provided with a thermometer. Tube *i* is at first brought into communication with the air by tap *h*, then the height of the barometer and temperature of the air is taken, and *i* connected with the burette by suitably turning the three-way tap. Part of the mercury is then withdrawn by tap *q*, and the air-bath heated to 300-310° C., until the level of the mercury remains constant. The apparatus is then allowed to cool down to the temperature of the room, when the original pressure is again established by adding mercury. The volume of gas is then read off and calculated for 760 mm. pressure and 0° C. The hydrogen may be measured either saturated with moisture, when a correction for the tension of the water vapour must be made, or by previously drying the gas. This is best done by taking a longer tube *i*, and placing over *k* a layer of strongly heated soda-lime.

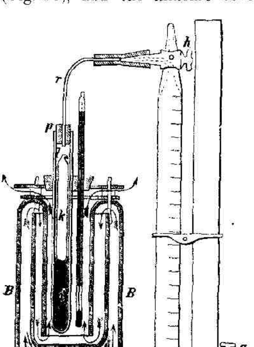


Fig. 50.

[1] *Liebig's Annalen*, 223, 269.

A. and *P. Buisine*[1] have shown that the reaction is not a quantitative one if a wax be heated directly with *potash-lime* (1 part of caustic potash and 2 parts of lime). They proceed, therefore, in the following way :—2-10 grms. of a wax, weighed accurately, are melted in a porcelain crucible, and an equal weight of finely powdered caustic potash stirred into the melted mass. The hard mass obtained on cooling is carefully powdered and intimately mixed with three parts of potash-lime for every part of wax weighed off. The mixture is filled into a test-tube or a pear-shaped flask, taking care that the vessel is nearly filled completely, and placed in an iron still, filled

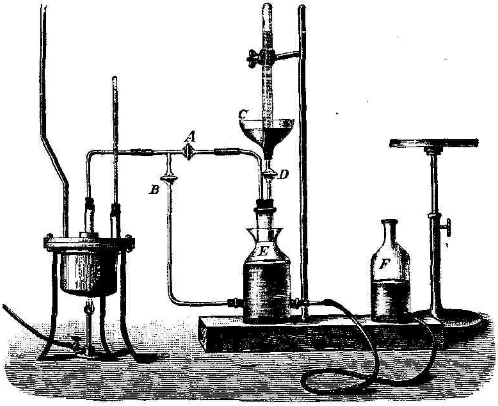


Fig. 51.

with mercury, and closed by a cover having three nozzles. Through one passes the outlet tube from the glass vessel containing the substance, whilst into the second is fixed a thermometer ; the third nozzle is provided with a long iron tube to condense and lead away the vapours of mercury.

Instead of collecting the gas in a *Hofmann* burette, *A.* and *P. Buisine* prefer to use the apparatus designed by *Dupré*, and shown in Fig. 51. The gas evolved can be made to enter the vessel E either from the top—by opening tap A—or from the bottom—by opening tap B. The glass tubes provided with the taps A and B are of small inner diameter. When all the connections have been made, bottle E is filled with water by raising bottle F until water enters C. Tap D is then closed, bottle F lowered, tap A opened, and the mercury

[1] *Monit. scientif.* 1890, 1127.

heated. At 180° C. the reaction commences; the temperature is, however, raised to 250° C. and kept thereat for two hours. If gas is liberated copiously the tap A is closed and B opened; thus it is easy to control and watch the progress of the reaction. When bubbles of gas no longer rise through the water, tap B is closed again and A opened. The apparatus is then allowed to cool down, and the gas introduced into the eudiometer, to be measured; the volume read off is calculated for 760 mm. pressure and 0° C.

Thus the volume of gas obtained for 1 grm. of substance is found. To take an example, in the case of myricyl alcohol the number of c.c. of hydrogen found is multiplied by 0·984.

If oleic acid be present the temperature should not be allowed to exceed 250° C., as otherwise palmitic acid may be formed with evolution of hydrogen.

Since cholesterol, if admixed with the aliphatic alcohol, remains practically unchanged, it can be obtained by extracting the powdered residue with ether in a *Soxhlet* extractor. Any solid hydrocarbons, which have not been separated beforehand by the above-described acetic anhydride method, will be extracted simultaneously with the cholesterol, and can now be separated from it by that method.

B. DETECTION AND DETERMINATION OF ADMIXED UNSAPONIFIABLE SUBSTANCES

If solid unsaponifiable substances like paraffin wax and ceresin have been admixed, they will be detected as described above, p. 377.

In manufactured products, as in "commercial stearine" or "Turkey-red oil," etc., lactones or anhydrides occur which may be mistaken for unsaponifiable matter. Due care must, therefore, be taken in such cases to guard against error ("Lactones," chap. viii. p. 339).

It should also be noted that waxes (which are only saponified with difficulty) may have escaped complete saponification, and thus be found amongst the unsaponifiable matter.

Considerable quantities of liquid unsaponifiable substances may be due to legitimate admixture, as in burning oils or lubricating oils (cp. chap. xv.), but in the majority of instances they constitute adulterants.

The liquid unsaponifiable substances may consist of either mineral oils, rosin oils, or tar oils, or a mixture thereof. In case only one kind be present, the specific gravity will supply the readiest means of identifying the liquid unsaponifiable matter, as will be gathered from the following table:—

Class of Oil.	Specific Gravity.
Heavy mineral oils	0·840-0·920
Rosin oils	0·960-1·01
Tar oils	Higher than 1·01

As regards **mineral oils**, I have placed the lower limit at 0·840, since the admixture of mineral oils of lower specific gravity is hardly practised to any appreciable extent, inasmuch as the specific gravity of an adulterated oil alone would reveal the presence of hydrocarbon oils of lower gravity. If mineral oils be present, the distillation products of crude petroleum, shale, and lignite, boiling from 250°-300°, of the specific gravity 0·855-0·900 (commercially obtainable as mineral lubricating oils), may be expected. Sometimes also higher boiling oils of the specific gravity 0·900-0·930 are met with in adulterated samples. The fractions boiling below 250°, such as those contained in a mineral burning oil, will only be found in small quantities; they are best detected by the flash point (see chap. xv.).

The specific gravity of **rosin oils**—*obtained by subjecting colophony* to destructive distillation and fractionating the distillate into "rosin spirit" and "rosin oil"—ranges as a rule from 0·96 to 0·99; but rosin oils having the specific gravity 1·01 are also met with in commerce. The chemical composition of the rosin oils is not yet fully understood; they consist mostly of hydrocarbons related to the terpenes, but contain also, according to the care exercised in distilling, larger or smaller quantities of rosin acids and other oxygenated substances, as shown in the third column of following table, giving the analysis of a number of commercial rosin oils ascertained in my laboratory:—

Commercial Rosin Oils (Lewkowitsch)

Rosin Oil.	Specific Gravity at 60° F.	Rosin Acids, calculated to Molecular Weight 346.
		Per cent.
"Soft"	0·9878	9·2
"Medium"	0·9946	26·3
"Hard"	0·9974	31·2
"	0·9877	19·6
"	0·9890	20·3
"	0·9982	18·6
"Siccative"	0·9955	4·9
"	1·0115	18·4

It should be noted that any rosin oils found in the unsaponifiable matter will be free from the rosin acids originally contained in the commercial oils, the rosin acids having combined with caustic potash to form soap in the saponification process. Therefore, if rosin oil has been detected, the original amount of admixed "rosin oil" was larger than the amount found by quantitative analysis. If no colophony was added to the sample under examination, then the amount of rosin acids can be determined by *Twitchell's* method (see p. 394). If, however, colophony also was added, then a very rough estimation only can be made by using some such numbers as are set out in the above table.

Tar oils (boiling between 240° and 350° C., and freed for the most part from naphthalene and anthracene by cooling, and from phenols by washing with caustic soda) are sometimes used as admixtures with lubricating oils. The specific gravities of these oils lie above 1·00.

Therefore, if tar oils constitute exclusively the unsaponifiable substance, the specific gravity test will most readily reveal its nature.

The indications furnished by the specific gravity test alone will, however, be of very limited value if a mixture of two of the described classes of oils, or even all three, be present. The following methods for further examination are available:—

The most reliable test for the detection of rosin oil in mineral oil is, as I can testify from my own experience, the *Liebermann-Storch* reaction:—

1 to 2 c.c. of the sample under examination are shaken, in a test-tube, with acetic anhydride at a gentle heat; after cooling, the acetic anhydride is drawn off by means of a pipette, and tested by adding *one drop of sulphuric acid of 1·53 specific gravity.*[1] *If rosin oil is* present, a fine violet (fugitive) colour is immediately produced.

If less than 1 to 2 c.c. are available, the test can be done on a watch-glass, by stirring the liquid with acetic anhydride and allowing a drop of sulphuric acid to run down the side.

It should be borne in mind that cholesterol also gives a similar colour reaction, and its presence may cause serious errors if due regard be not paid to this similarity. If, therefore, cholesterol[2] be suspected, a rapid method to prove the presence of rosin oil would be to examine the mixed fatty acids, obtained from the soap solution, for rosin acids (see below), which always accompany rosin oils. A *more complicated method would be to separate the cholesterol as* benzoate.

If rosin oil has been detected, and the specific gravity found below 0·96, then admixture with oils belonging to the first class may be suspected. The quantitative determination of the mineral oil, in admixtures of mineral oil and rosin oils, is of practical importance in the examination of lubricating oils. The methods hitherto elaborated will be described under the heading "Lubricating Oils" in Chapter XV.

If rosin oils be absent, and the specific gravity be above 0·920, then the presence of tar oils is proved. The latter may be detected *by the aid of nitric acid, specific gravity 1·45.*[3] Tar oils exhibit a decided rise of temperature on mixing with the acid, whereas pure mineral oils become but very slightly warmer. It is best to ascertain *by a preliminary test whether a violent reaction* takes place or not, the size of apparatus to be chosen depending on the result. 7·5 c.c. of the sample are placed in a graduated tube, cooled to 15° C., and

[1] This acid contains 62·53 per cent of SO_4H_2; it is prepared by mixing 34·7 c.c. of conc. sulphuric acid with 35·7 c.c. of water.

[2] Green fluorescence of the liquid, after the violet colour has disappeared, points to the presence of isocholesterol.

[3] Breukers, *Zeit. f. analyt. Chemie*, 1879, 546.

7·5 c.c. of nitric acid., spec. grav. 1·45, of the same temperature, added. The tube is closed by a cork, provided with a thermometer, and the contents are shaken thoroughly. The rise of temperature is then read off. If a strong reaction has been found to take place, a large, strong-walled bottle must be employed, and the cork, besides holding the thermometer, must be fitted with an open glass tube, which may be closed by the finger whilst shaking. It is, however, advisable to employ small quantities, and to proceed as in *Maumené's* temperature reaction test (see p. 314). The same reaction has been proposed by *McIlhiney*[1] for the detection of rosin oil in a mixture of this oil with mineral oils.

The qualitative detection of rosin oils by means of their optical rotation will be dealt with under the headings "Linseed Oil" (chap. xiv.) and "Lubricating Oils" (chap. xv.).

[1] *Journ. Amer. Chem. Soc.* 16, 385.

CHAPTER X

DETECTION AND QUANTITATIVE DETERMINATION OF ROSIN

i. Properties of Rosin

Common rosin or colophony is the residue obtained on heating pine rosin in a still until all the moisture and the oil of turpentine is distilled off. The distillation is frequently supported by passing a current of steam through the heated mass. After driving off the "oil of turps," the steam is shut off and the melt in the still heated for some little time so that the mass may become completely amorphous, after running off into casks, in which it solidifies. Colophony forms a light yellow to dark brown transparent mass, the colour depending on the manner in which the distillation has been conducted and on the temperature employed.

In commerce French rosin is known by the name "galipot." The various qualities of American rosin are distinguished by the letters of the alphabet, A being almost black, the brands then gaining in paleness and transparency until, as the letters ascend in the alphabet, they reach with the letter W, or W.G. (water glass), or W.W. (water white), the palest and most transparent qualities.

Rosin possesses vitreous lustre, and is very brittle, breaking with shallow conchoidal fracture. The specific gravity of colophony or common rosin—or shortly "rosin"—varies from 1·045 to 1·085 at 15° C. The melting point of different rosins varies considerably, depending on the amount of rosin oil in the colophony. Some varieties soften at 70° C., and become semi-fluid in boiling water; others melt at 99°-100° C., or even at 120°-140° C. Rosin does not melt, however, to a clear liquid like fats or fatty acids. On warming, rosin emits a pleasant terebinthinate odour; at a higher temperature, in contact with air, it burns with a dense yellow and sooty flame, sending forth a very characteristic smell.

On subjecting rosin to destructive distillation, rosin spirit and rosin oils are obtained as distillates, and coke is left behind. Distilled *in vacuo* it yields a hydrocarbon (colophene?) and an acid $C_{30}H_{32}O_2$ (isosylvic acid).[1] Rosin is insoluble in water, dissolves easily in alcohol, 1 part of rosin requiring only 10 parts of 70 per

[1] Bischoff and Nastvogel, *Berichte* 1890, 1919; *Journ. Soc. Chem. Ind.* 1890, 927.

cent alcohol for complete solution. The alcoholic solution has acid reaction; the acid can be neutralised by titration with alkali, using phenolphthalein as an indicator. Rosin is also soluble in methyl *alcohol, amyl alcohol, ether, benzene, acetone, chloroform,* carbon bisulphide, and oil of turpentine. Most of its constituents also dissolve in petroleum spirit, the percentage of insoluble varying from 1 to 20 per cent in different samples. Solutions of rosin do not leave a grease-spot on paper.

Colophony also contains varying quantities of "unsaponifiable matter," viz. hydrocarbons, due to the partial breaking up of the acid on distilling pine rosin. The following amounts of "unsaponifiable matter" show how widely different in this respect commercial rosins are:—

Origin.	Unsaponifiable.	Observer.
	Per cent.	
French	15·2	Jean
American "W.W." .	7·34	Evans and Black
" "W.G." .	5·00	"
" "N." . .	9·00	"
" "N." . .	8·21	"
" "M." . .	7·61	"

The quantitative methods used in the analysis of oils and fats have also been applied to the examination of rosin, since rosin is frequently found in admixture with oils, fats, and waxes, and the commercial products derived therefrom. The examination and determination of rosin is of especial importance in the analysis of soaps. In the following table I have collated some numbers obtained in the manner described under the headings "Neutralisation Number," "Saponification Number," etc. It should, however, be distinctly *understood that these numbers can only* be looked upon as marking the limits within which a given sample may fall. It may be stated, as a general rule, that the darker the rosin the smaller is the difference of saponification and neutralisation values, as shown by Column III. of the table:—

Kind of Rosin.	I. Neutralisation Value.	II. Saponification Value.	III. Difference, II.-I.	IV. Iodine Value.	Observer.
Austrian . .	146·0	167·1	21·1	116·8	v. Schmidt and Erban [1]
,, . .	130·4	146·8	16·4	109·6	,,
Austrian, pale .	163·0	...	...	...	Kremel [2]
,, dark .	151·0	...	...	...	,,
American . .	173·0	...	...	...	,,
,, . .	169·0	...	...	...	,,
Refined . . .	181·0	...	...	178·9 [3]	Mills [4]
American "W.W."	154·1	183·6	29·5	92·4-93·5	Lewkowitsch [5]
,, "W.G.".	161·4	178·9	17·5	113-114	,,
,, "W.G.".	163·3	184·3	21·0	104-107	,,
,, "W." .	164·3	194·3	30·0	62-64	,,
,, "V." .	164·6	194·0	30·0	55-58	,,
,, "F." .	159·0	174·7	15·7	111-113	,,
Galipot . . .	*138·65*	*174·76*	*36·11*	*121·5-123·5*	,,
American "F." .	153·8-169·4	165·2-176·1	5·5-11·8	...	Weger
,, "N." .	157·3	174·3	17·0	168·4 [6]	Smetham and Dodd
,, "W.G.".	160·1	177·3	17·2	165·9	,,
,, "W.W."	154·5	174·3	19·8	158·5	,,
,, "Wite".	160·8	177·6	16·8	184·7	,,
,, "*Nemo*"	*162·0*	*176·4*	*14·4*	*181·0*	,,

McIlhiney showed that the iodine number varied with the time allowed for the absorption, and with the excess of iodine used to a much greater extent than is the case with oils and fats, and therefore concluded that the *Hübl* process did not furnish useful results in the examination of rosin. This is indeed borne out by the numbers given in the two following tables :—

Iodine Absorption of Rosin from Hübl Solution[7]

	Iodine Number (Hübl).			
	After 2 hours.	After 4 hours.	After 18 hours.	After 7 days.
Rosin "W.W." . .	115·5	124·1	158·5	
,, "N." . .	114·3	125·3	168·4	165·3
,, "W.G." . .	115·5	121·7	165·9	

[1] *Journ. Soc. Chem. Ind.* 1889, 308. [2] Wagner's *Jahresbericht*, 1886, 443.

[3] Calculated from the bromine value 112·7 by multiplying by $\frac{127}{80}$.

[4] *Journ. Soc. Chem. Ind.* 1886, 222.

[5] *Journ. Soc. Chem. Ind.* 1903, 505, and *Unpublished Experiments.* These iodine numbers were determined with Hübl's solution, which was allowed to act for six hours.

[6] Hübl iodine solution was used and allowed to act for eighteen hours, *Journ. Soc. Chem. Ind.* 1900, 101.

[7] Smetham and Dodd, *Journ. Soc. Chem. Ind.* 1900, 101.

Iodine Absorption of Rosin from Wijs' Solution

	Time.	Absorption.	Observer.
Rosin "N."	10 minutes	171·2	Smetham & Dodd
	20 ,,	177·5	,,
	30 ,,	183·6	,,
	1 hour	194·8	,,
	18 hours	249·4 ; 249·4	,,
	48 ,,	270·5	,,
Rosin "N."	2 hours	165·3	Lewkowitsch
	24 ,,	172·2	,,
,, "W."	2 ,,	159·9	,,
	24 ,,	195·8	,,
,, "W.G."	2 ,,	219·0	,,
	10 ,,	214·2	,,
	18 ,,	216·0	,,
	24 ,,	237·7	,,

McIlhiney[1] prefers, therefore, to apply the bromine absorption method described above (chap. vi. p. 239) to the examination of rosin. From the results obtained with two specimens of rosin ("W.G." and "E."), *McIlhiney* concluded that the bromine is entirely taken up by substitution. Hence the bromine *addition value* of rosin would be practically *nil*. In further support of his contention that the bromine absorption numbers for rosin lead to more definite numbers than the iodine absorption by *Hübl's* process, *McIlhiney*[2] published recently some numbers which I collate in the following table. In order to show the discrepancy between the bromine and the iodine numbers more clearly, I have calculated in Column II. the observed bromine absorption numbers to iodine numbers, by multiplying them by $\frac{127}{80}$.

Bromine Absorption of a Sample of American Rosin, "W.G."

Time.		Bromine Absorption. I.	II.	III. Iodine Absorption. Per cent.
		Experiment. Per cent Bromine.	*Calculated to Iodine Absorption.*	(Found by Hübl's Method.)
hours.	mins.			
0	2	160·8	255·3	
0	18	174·5	277·0	
1	0	...	...	126·7
1	9	178·0	282·6	
2	0	...	...	133·1
4	0	...	...	142·0
8	0	...	...	144·8
18	0	...	...	160·3
20	0	213·4	338·8	
52	0	..	...	172·6

[1] *Journ. Soc. Chem. Ind.* 1894, 668. [2] *Journ. Amer. Chem. Soc.* 1902, 1109.

Experiments made in my laboratory, however, show that commercial rosins do possess, besides substitution numbers, definite addition numbers, as will be gathered from the following table, to which I have added, for the sake of comparison, the iodine absorption numbers found by the *Wijs'* modification of the *Hübl* method.

Unfortunately, on using the *Wijs'* solution substitution numbers cannot be ascertained, as acetic acid acts on potassium iodate in a very different manner from mineral acids, widely varying results being obtained as the concentration and the time the acetic acid is allowed to act on the iodate varies.

Bromine and Iodine Absorptions of Common Rosins (Lewkowitsch)

Rosin.	Bromine Values.			Time. Acted on by Bromine.	Iodine Value. (Wijs' Solution.)			
	Total Absorption.	Addition.	Substitution.		After 2 hours.	After 10 hours.	After 18 hours.	After 24 hours.
"W.G."	210·7	41·14	84·78	½ hour	219·0	214·2	216·0	237·7
	211·6	49·68	80·96	,,				
	202·5	59·92	71·29	1 hour				
	203·5	88·42	57·54	,,				
"N."	146·9	87·6	29·65	½ hour	165·3	...	...	172·2
	145·7	108·06	18·82	,,				
	148·1	92·84	27·63	1 hour				
	145·2	107·7	18·75	,,				
"W."	201·8	114·0	43·9	½ hour	159·9	...	...	195·8
	201·6	104·96	48·42	,,				
	197·2	78·24	59·48	1 hour				
	191·8	85·14	53·33	,,				

The high neutralisation values prove conclusively that colophony is not, as *Maly* maintained, an anhydride, viz. abietic anhydride, but consists chiefly of free acids and small quantities of anhydrides.

The same conclusion has been arrived at by *Perrenoud*.[1] According to this author colophony does not contain any abietic anhydride. In the case of American colophony (from trunks of *Pinus Strobus* and *Pinus Picea*, and from the root of *Pinus sylvestris*) the crystals are said to be *abietic* acid, whereas in "galipot" and in rosin from the trunk of *Pinus sylvestris* they are stated to consist of the isomeric *pimaric* acid. Both acids have the same formula: $n(C_{10}H_{14}O)$; that of pimaric acid, as determined by the analysis of a crystalline ammonium salt, is most likely $C_{40}H_{56}O_4$. Both abietic and pimaric acids are optically active, and rotate the plane of polarised light to the left. The specific rotatory powers of abietic and pimaric acids are stated by *Perrenoud* to be 48° and 56° respectively.

[1] *Chem. Zeit.* 1885, 1590.

The *sylvic* acid of some authors is in *Liebermann's*[1] opinion identical with abietic acid. His researches, continued by *Haller*,[2] led to the result that pimaric acid is optically inactive. *Vesterberg*,[3] again, is of the opinion that three distinct acids are coexistent in "galipot."

Looking at these partly contradictory views on the ultimate composition of colophony, it is not surprising to find that *Mach*[4] rejects the formulæ given for abietic, sylvic, and pimaric acids. He states that these acids are identical, and proposes for *abietic acid* (the name he retains) the formula $C_{19}H_{28}O_2$, which he derived from numerous ultimate organic analyses and determinations of the molecular weight of specimens of the acid prepared by different methods from various samples of colophony. According to *Fahrion*,[5] *Mach's* abietic acid is identical with sylvic acid $C_{20}H_{30}O_2$.[6]

Abietic acid, $C_{44}H_{64}O_5$ [*Maly*], or $n(C_{10}H_{14}O)$ [*Perrenoud*], or $C_{19}H_{28}O_2$ [*Mach*], is obtained in a pure state in the form of crystals by digesting 1 part of coarsely powdered colophony with 2 parts of 70 per cent alcohol at a temperature of 50°-60° C. The crystalline powder which separates is purified by recrystallisation from 3 parts of boiling alcohol of the same concentration. Another method is to pass hydrochloric acid gas through an alcoholic solution of colophony, when abietic acid separates (Flückiger, *Jahresberichte der Chemie*, 1867, 727). According to *Mach*, abietic acid occurs in colophony in varying amounts; some specimens contain 90 per cent of the crude acid, from others no acid could be isolated. On treating an alcoholic solution of colophony with water, a precipitate of impure abietic acid is obtained, which remains suspended in the liquid, forming with it an emulsion. On adding a dilute mineral acid and on warming, rosin separates in the form of globules on the side of the containing vessel, so that the clear liquid may be poured off. The rosin thus obtained is at first very viscid, but regains its former consistence by being boiled repeatedly with water, or on heating to incipient fusion. In its pure state abietic acid crystallises in laminæ or small crystals, melting at 165° C.; they are soluble in alcohol, ether, benzene, and glacial acetic acid. Abietic acid is not converted into an anhydride on heating.

Abietic acid is a dibasic acid. On warming colophony with dilute caustic alkalis, it is readily dissolved with formation of salts—rosinates or pinates—that resemble in many respects the ordinary soaps. For this reason these salts are termed "rosin soaps." Thus the solutions of the alkali salts lather on being agitated, and the "rosin soaps" are thrown up from their aqueous solutions by addition of concentrated alkali or of common salt. This separation, however, does not take place so readily and completely as in the case of the soaps made from

[1] *Berichte*, 17. 1885.
[2] *Ibid.* 18. 2167.
[3] *Ibid.* 18. 3334.
[4] *Journ. Soc. Chem. Ind.* 1893, 1044.
[5] *Zeit. ang. Chem.* 1901, 1197; 1902, 83. Cp. also Henry, *Journ. Chem. Soc.* 1891, 1144; Tschirch and Studer, *Arch. d. Pharm.* 1903 (241), 495, 523.
[6] Cp. Tschirch and Studer, *Arch. d. Pharm.* 241, 495; and Fahrion, *Zeit. ang. Chem.* 1904, 239.

fatty acids. Dilute mineral acids liberate the free rosin acids from their soaps.

The sodium salt dissolves readily in alcohol, and also in ether containing alcohol; in pure ether, however, it is but sparingly soluble. According to experiments by *Barfoed*, 29 c.c. of ether dissolved within twenty-four hours 0·0239 grm., and 19 c.c. after eight days 0·041 grm. of sodium rosinate.

The solutions of the rosinates of the alkali metals give precipitates with solutions of the salts of the alkaline earths and heavy metals. On the solubility of some of these salts in alcohol and ether, methods of separating the rosin acids from the fatty acids have been based. The zinc, copper, silver, and manganese rosinates are soluble in ether; calcium rosinate is insoluble in this menstruum (cp. chap. xv.).

In the quantitative analysis of a rosin soap the acid is separated as free rosin acid (abietic acid), and it would therefore be necessary in very accurate analysis (as will be shown later under "Analysis of Soaps") for the proper calculation of the composition of soap to convert the weight of the rosin acids into the weight of the original colophony. From the table[1] it will be seen that rosin can be determined by titration with standard alkali solutions. This is best done in alcoholic solution. Calculating from the formula $C_{44}H_{64}O_5$, it would follow that 672 parts of abietic acid combine with 112·2 parts of potassium hydrate to form a neutral rosinate. Hence, for 56·1 parts of potassium hydrate, there would be required 336 parts of abietic acid. Since colophony contains some anhydrides besides free acid, the mean combining weight of rosin acids may be taken for practical purposes as 346. From the formulæ for abietic acid, $C_{44}H_{64}O_5$, and for the anhydride, $C_{44}H_{62}O_4$, it follows that 100 parts of rosin acid are equivalent to 97·32[2] parts of anhydride, but since rosin only contains 10-20 per cent of anhydrides, as will be seen from Column III. of the table, p. 388, the weight of the separated rosin acids will only exceed that of the original rosin by 0·3-0·4 per cent, which falls within the limit of errors in practical analysis.

Some further light has been thrown on this by some experiments made by *Smetham* and *Dodd*, who saponified rosin with an excess of aqueous caustic soda, decomposed the resulting soap with a slight excess of dilute sulphuric acid, and separated the insoluble rosin acids by means of ether.[3] In the following table I collate the neutralisation and saponification numbers of the original rosins with those recovered after having passed through the saponification process:—

[1] P. 388.

[2] Pending a confirmation of *Mach's* observations, these figures are still retained.

[3] Cp. also Henriques, *Chem. Rev.* 1899, 110.

[TABLE

Kind of Rosin.	Original Rosin.			Recovered Rosin after Saponification.		
	Neutralisation Value.	Saponification Value.	Difference.	Neutralisation Value.	Saponification Value.	Difference.
American "N." . .	157·3	174·3	17·0	159·1	165·5	6·4
,, "W.G." .	160·1	177·3	17·2	161·0	169·5	8·5
,, "W.W." .	154·5	174·3	19·8	159·1	167·5	8·4
,, "Wite" .	160·8	177·6	16·8	163·9	176·4	12·5
,, "Nemo" .	162·0	176·4	14·4	163·9	175·3	11·4

ii. Detection and Determination of Rosin in Neutral Fats and in Waxes

The older methods based on the ready-solubility of rosin in alcohol do not lead to satisfactory results. The most reliable method for the detection of rosin, which I recommend as thoroughly trustworthy, is the *Liebermann-Storch* reaction described above (p. 384). In case the samples are too deeply coloured to show the colouration distinctly, it is advisable to saponify the sample with alcoholic potash and liberate the fatty acids together with the rosin acids by acidulating, and to examine the mixed acids.

To perform the test, the fatty acids are dissolved in acetic anhydride at a gentle heat and the solution cooled. Sulphuric acid of 1·53 sp. gr.[1] is then carefully allowed to flow into the solution, when the presence of the minutest quantity of rosin acid will be indicated by the appearance of a reddish-violet colouration; if the solution be too warm, this colour will disappear almost immediately, changing into a brownish-yellow. In any case, the colour disappears quickly. Fatty acids do not produce the violet colour; but it should be remembered that cholesterol, which gives a similar reaction with acetic anhydride and sulphuric acid, might be present amongst the mixed acids. In the latter case the cholesterol, previous to the liberation of the mixed fatty acids, must be removed by shaking out the soap solution with ether. This reaction may be also used for the detection of rosin in beeswax.

In mixtures of neutral fats with rosin—as linseed oil and rosin—the writer determines approximately the rosin by titrating an accurately weighed quantity of the sample dissolved in ether-alcohol with standard alkali, using phenolphthalein as an indicator. The combining weight adopted for rosin is 346, and the amount of free fatty acids in the oil is, of course, neglected, being, as a rule, very small compared with the acid value corresponding to the rosin. Experiments carried out on mixtures of linseed and cotton seed oils with rosin gave very accurate results.

[1] Sulphuric acid of 1·53 sp. gr. contains 62·53 per cent of SO_4H_2; it is prepared by mixing 34·7 c.c. of conc. sulphuric acid with 37·5 c.c. of water.

If greater accuracy be desired, the rosin acids are isolated together with the mixed fatty acids, and examined as described under the *following head* :—

iii. Quantitative Determination of Rosin Acids in Admixture with Fatty Acids

Lewkowitsch[1] has shown that the older methods proposed by *Barfoed*, *Gladding*, and the modifications thereof, do not lead to reliable results. A description of these methods is, therefore, omitted here. Recently a combination of *Gladding's* method with *Twitchell's*, the one described below, has been proposed by *Holde*.[2] But since the corrections suggested appear to me somewhat arbitrary, this method also is omitted here.[3]

Twitchell's[4] method is based on the property aliphatic acids possess of being converted into their ethylic esters when acted upon by hydrochloric acid gas in their alcoholic solution, whereas colophony practically undergoes little change under the same treatment, abietic acid separating from the solution (see p. 391). The analysis is carried out as follows :—

Two to three grams of the mixed fatty and rosin acids are weighed off accurately, dissolved in a flask in ten times their volume of *absolute* alcohol (90 per cent alcohol must not be used, as the conversion of fatty acids into esters is not complete in that case), and a current of dry hydrochloric acid gas passed through, the flask being cooled by immersion in cold water. The gas is rapidly absorbed at first, and after about forty-five minutes, when unabsorbed gas is noticed to escape, the operation is finished. To ensure complete esterification the flask is allowed to stand for an hour, during which time the ethylic esters and the rosin acids separate on the top as an oily layer. The contents of the flask are then diluted with five times their volume of water, and boiled until the aqueous solution has become clear. From this stage the analysis may be carried out either (*a*) volumetrically or (*b*) gravimetrically.

(*a*) *The Volumetric Analysis.*—The contents of the flask are transferred to a separating funnel, and the flask rinsed out several times with ether. After vigorous shaking the acid layer is run off, and the remaining ethereal solution, containing the ethylic esters and the rosin acids, washed with water until the last trace of hydrochloric acid is removed. 50 c.c. of alcohol are then added, and the solution titrated with standard caustic potash or soda, using phenolphthalein as an indicator. The rosin acids combine at once with the alkali, whereas the ethylic esters remain practically unaltered. Adopting as the combining equivalent for rosin 346, the number of c.c. of

[1] *Journ. Soc. Chem. Ind.* 1893, 503.
[2] *Mitteil. a. d. Königl. Techn. Versuchsanst*, 1902, 41.
[3] For the description of the earlier quantitative methods, the reader is referred to the second edition of this work.
[4] *Journ. Soc. Chem. Ind.* 1891, 804.

normal alkali used multiplied by 0·346 will give the amount of rosin in the sample.

(*b*) *The Gravimetric Method.*—The contents of the flask are mixed with a little petroleum ether, boiling below 80° C., and transferred to a separating funnel, the flask being washed out with the same solvent. The petroleum ether layer should measure about 50 c.c. After shaking, the acid solution is run off, and the petroleum ether layer washed once with water, and then treated in the funnel with a solution of 0·5 grm. KOH and 5 c.c. of alcohol in 50 c.c. of water. The ethylic esters dissolved in the petroleum ether will then be found to float on the top, the rosin acids having been extracted by the dilute alkaline solution to form rosin soap. The soap solution is then run off, decomposed with hydrochloric acid, and the separated rosin acids collected as such, or preferably dissolved in ether and isolated after evaporating the ether. The residue, dried and weighed, gives the amount of rosin in the sample.

Of all the methods proposed hitherto for the estimation of rosin acids in mixtures with fatty acids, *Twitchell's* process yields the best results. They must not, however, be considered as strictly correct; they are only approximate, as *Lewkowitsch*[1] has shown by an exhaustive examination of both the volumetric and gravimetric processes.

Since the mean combining weights of different brands of commercial rosin vary within considerable limits (cp. p. 388), an uncertainty adheres to the volumetric analysis of which the gravimetric analysis is free. Under the action of the hydrochloric acid the rosin appears to undergo some destruction[2] with the formation of acids of lower molecular weight, since the volumetric analysis gave, as a rule, too high results. In the gravimetric process, again, some of these secondary products pass into the aqueous solution without being dissolved by the petroleum ether. By a subsequent extraction with ether, part of the dissolved substances may be recovered, but even then the results of the gravimetric analysis were found too low. Of course the unsaponifiable oils occurring in rosin (p. 387) remain in the petroleum ether solution and thus escape weighing. But even this cannot wholly account for the great deficiency.

The subjoined tables, giving the analysis of mixtures of oleic acid

[1] *Journ. Soc. Chem. Ind.* 1893, 504.

[2] The results given in table, p. 396, are confirmed by experiments made since by *Evans* and *Black*, as shown by the following table:—

Weight of Rosin.	Rosin calculated from Titration.	Loss.
Grms.	Grms.	Per cent.
2·0968	2·054	2·00
2·4728	2·45	0·90
2·085	..	0·93
2·08	..	0·69
2·115	..	1·14

and rosin acids of previously ascertained combining weight, will confirm the writer's critical remarks :—

Volumetric Analysis (Lewkowitsch)

Oleic Acid.	Rosin.	1/1 KOH used.	Mixture contains Rosin Acids. Combining Weight 346.		Calculated for the yield of Rosin Acids only.	
			Theory.	Experiment.	Theory.	Experiment.
Grms.	Grms.	c.c.	Per cent.	Per cent.	Per cent.	Per cent.
2·5096	0·8027	2·4	24·234	24·90	100·0	100·60
2·3988	0·8167	2·56	25·398	27·35	100·0	105·50
1·5638	1·5532	4·41	49·83	48·40	100·0	95·60
1·4006	1·5202	4·19	52·047	48·93	100·0	92·81
0·8918	2·5198	6·68	73·86	66·397	100·0	89·47
0·8296	2·5298	6·72	75·305	67·81	100·0	89·45

Gravimetric Analysis (Lewkowitsch)

No.	Oleic Acid.	Rosin.	Found Rosin Acids.	Mixture contains Rosin Acids.		Calculated for yield of Rosin Acids.	
				Theory.	Experiment.	Theory.	Experiment.
	Grms.	Grms.	Grms.	Per cent.	Per cent.	Per cent.	Per cent.
1	2·4666	0·8199	0·7385	24·947	22·32	100	87·65
2	2·8058	0·8577	0·7736	23·412	20·98	100	87·80
3	1·6465	1·5342	1·3200	48·234	40·96	100	83·73
4	1·4090	1·5092	1·3128	51·716	44·35	100	84·65
5	0·8600	2·5252	2·0930	74·595	60·58	100	80·66
6	0·8430	2·5322	2·1744	75·023	63·12	100	83·56
7	...	4·2524	3·5631	...	...	100	83·44
8	...	4·6864	3·8334	...	...	100	81·46
9	...	4·6700	3·8979	...	...	100	83·12

The following tables will give an indication as to how far, in practical cases, the results obtained by either process approach the theoretical ones.

The "mixed fatty and rosin acids" were obtained from soaps specially prepared on a large scale from carefully weighed quantities of fats and rosins. Average samples of the fats and the rosins were examined separately for the yield of fatty acids from the former and for the combining weight of the latter, these determinations being *indispensable for a correct* calculation of the theoretical amount of rosin acids.

[TABLE

Volumetric Analysis (Lewkowitsch)

Mixed Fatty and Rosin Acids.	Rosin Acids.	
	Theory.	Experiment.
No.	Per cent.	Per cent.
1	9·79	9·98, 9·34, 9·795, 9·91.
2	19·69	23·97, 24·55, 22·93, 23·28, 23·98, 24·08.
3	21·45	24·96, 24·78, 23·63.
4	24·66	24·89, 25·15, 25·06, 24·28.
5	30·31	29·69, 30·12, 28·18, 29·78.
6	39·81	40·24, 40·37, 41·44, 42·13, 41·8, 40·37, 42·18, 40·55, 40·07, 40·05, 43·69, 41·12, 41·81, 40·77, 44·82.
7	45·05	45·76, 46·50, 49·61, 47·66, 46·45, 47·84, 45·34, 44·24, 44·48, 44·39.

Gravimetric Analysis (Lewkowitsch)

Mixed Fatty and Rosin Acids.	Rosin Acids.	
	Theory.	Experiment.
No.	Per cent.	Per cent.
1	9·79	9·38, 9·97.
2	19·69	20·46, 20·55, 19·96,[1] 19·99, 19·44, 19·33.
3	21·45	19·25, 18·27, 19·37, 17·83,[1] 19·54, 18·61, 18·57, 19·16.
4	24·66	20·97, 16·65, 21·76.
5	30·31	25·76, 25·06, 23·66, 26·10.
6	39·81	35·97, 38·86, 36·44, 36·14, 35·42, 35·86, 32·51, 36·29.
7	45·05	37·58, 37·23, 37·29, 36·97, 35·32, 40·06, 36·8.

By washing the petroleum ether solution with alkali a second time, and extracting the acid layer with common ether, the following results were obtained :—

[1] Emulsion.

[TABLE

Mixed Fatty and Rosin Acids.	Rosin Acids.				
	Theory.	Experiments.			
		Extracted by First Alkali Wash.	Extracted by Second Alkali Wash.	Extracted by Ether.	Total.
No.		Per cent.	Per cent.	Per cent.	Per cent.
2	19·69	19·46	0·115	1·045	20·62
2	*19·69*	*18·44*	*0·074*	*0·822*	*19·34*
3	21·45	19·14	0·105	0·3615	19·607
3	21·45	19·19	0·061	0·2839	19·54
4	24·66	21·72	0·179	1·203	23·102
4	24·66	22·29	0·239	1·01	23·54
5	30·31	25·75	0·019	2·41	28·18
5	30·31	26·93	0·085	0·72	27·73
6	39·81	34·96	1·296	1·567	37·80
6	39·81	34·596	0·190	1·12	35·91

In case the rosin admixed originally with the fat contained notable quantities of (unsaponifiable) rosin oils, the latter are determined as described under the following heading:—

iv. Quantitative Determination of Rosin Acids in Admixture with Fats (or Fatty Acids) and Unsaponifiable Matter

If a mixture of rosin acids, fat, and unsaponifiable matter be under examination, the sample is saponified by boiling with alcoholic potash, and the alcohol driven off by prolonged boiling after diluting with water. The aqueous solution of soap is then transferred to a separating funnel — regardless of any undissolved unsaponifiable matter—and shaken out with petroleum ether, whereby the unsaponifiable matter is removed. The soap solution yields, on treatment with a mineral acid, a mixture of fatty and rosin acids, which are separated by *Twitchell's* process.

By using *Twitchell's* volumetric method the separation of the unsaponifiable matter may be avoided by the following procedure:[1]—The mixture is saponified with alcoholic potash, and the rosin acids, fatty acids, and unsaponifiable matter isolated by acidulating. If a mixture of the acids and unsaponifiable matter be given at the outset, the saponification, of course, is unnecessary.

Two grams of the mixed acids and unsaponifiable matter are weighed off accurately, titrated with normal caustic soda or potash, and the number of c.c., used until neutrality to phenolphthalein is reached, noted. Another 2 grms. are treated with hydrochloric acid gas, as described above, and titrated with normal alkali. If a be the number of c.c. used in the first experiment, and b the number found in the second experiment, then we shall find, adopting as the combining

[1] *Journ. Soc. Chem. Ind.* 1891, 804.

weight for rosin 346, and for fatty acids (palmitic, stearic, oleic) 275—

1. Weight of rosin acids $= a \times 0{\cdot}346$
2. Weight of fatty acids $= (a - b) \times 0{\cdot}275$
3. Weight of unsaponifiable $= 100 - [a \times 0{\cdot}346 + (a - b) \times 0{\cdot}275]$.

The accuracy of the result will, of course, largely depend on the correctness of the assumed combining weights 346 and 275.

v. Separation of Rosin from Fatty Acids

The separation of rosin acids from fatty acids is effected by passing the mixture of rosin and fatty acids through the esterification process described under *Twitchell's* method. We then have a mixture of free acids and esters, and after titration, as *e.g.* in the volumetric process, there results a mixture of rosin soap and ethyl esters of the fatty acids. Now, if the alcohol is distilled off and the remaining mixture is treated with water, the soap is dissolved, leaving the esters floating on the surface of the soap solution. The two layers are separated, and the soap solution, after washing with common ether to remove the last traces of dissolved ethylic esters, yields on acidulating the rosin acid. The ethylic esters are saponified by means of caustic alkali, and the fatty acids separated in the usual manner. Both the rosin and the fatty acids may then be examined separately.

CHAPTER XI

APPLICATION OF THE FOREGOING METHODS TO THE SYSTEMATIC EXAMINATION OF OILS, FATS, AND WAXES

An attempt is made in this chapter to describe in what manner the methods detailed in the foregoing chapters can be employed in the examination of a given sample, with a view to identifying it, or to determine its nature. It may be stated at the outset that in the present state of our knowledge we are not yet in possession of a definite course of analysis to be followed in all circumstances, as is the case in inorganic analysis. Yet by adopting a systematic plan of examination, it is possible in the majority of cases to identify a given sample of oil, fat, or wax, or to ascertain whether it is a pure or adulterated specimen. In the latter case the nature of the adulterant can generally be ascertained.

The **consistence** at the ordinary temperature helps to limit conveniently the range of substances to which examination may extend.

Colour also proves in many cases of some assistance, chiefly in the case of solid fats, since most oils in their refined state have a bright yellow colour. Thus amongst the solid fats laurel oil will be recognised by its yellowish-green colour; crude palm oil will always be distinguished by its red colour, shading off from the brightest red of Lagos oil to the dark red of Congo oil; shea butter, again, by its grey or greenish-grey colour, and beeswax by its characteristic dirty yellow colour.

The **odour** and also the **taste** of a sample will, as a rule, give some clue as to its nature. The "organoleptic" methods require, however, a good deal of practical experience, which is more frequently possessed by dealers in oils than by analytical chemists. Still, it is easy to discriminate the marine animal oils from other oils by their characteristic smell. Also rape oil, olive oil, lard oil, cotton seed oil, linseed oil, are readily recognised by their smell, especially when slightly warmed. It is even possible in some cases to recognise adulterants, such as rosin, or even mineral oils. Greater practice is required for the recognition of certain oils or fats by **taste**; linseed oil, maize oil, cotton seed oil, can be recognised thereby. Also lard and tallow can be readily identified. The recognition of *rancidity by taste* in the case of the edible oils and fats is of great im-

portance, the taste alone being the ultimate criterion in deciding whether a sample is rancid or not. A cultivated sense of taste is required for the giving of an opinion as to the value of a particular brand of edible oil that is pure in the sense of being wholly free from adulterants. To take an example, taste alone can discriminate between the fine olive oils of Tuscany and the harsher oils of South-Eastern Italy.

If a mixture of two oils is under examination, the preliminary indications furnished by consistence, colour, etc., frequently lose their importance. Yet with the help of the methods described in the foregoing chapters, it is, as a rule, possible to detect the presence of either constituent of the mixture, at least qualitatively. Frequently it will even be feasible to determine quantitatively the proportions in which the oils have been mixed.

A more difficult problem is presented by a mixture of three or more oils or fats. In cases of this kind commercial analysis may not always lead to a satisfactory result; still it will be possible to identify at least one or two of the individual constituents in a mixture.

Correct interpretation of indications afforded by the tests applied and strict logical reasoning, enable us in the majority of cases to so narrow down the range of possible constituents of the mixture that the practised analyst will but rarely be confronted with the impossibility of arriving at approximate accuracy at least. If in the course of a commercial analysis the limits of our present knowledge have been reached, the application of methods that have not been used for the case under consideration will suggest themselves. This may happen in the examination of technical products derived by processes described under Chapter XV., and frequently the analysis will have to approximate to the nature of an investigation.

One of the most important problems required to be solved by commercial analysis is whether a sample is pure or sophisticated.

Adulteration of saponifiable oils and fats with unsaponifiable oils or solid hydrocarbons will be the easiest to detect. The object of sophistication being, of course, to cheapen an article of high price, those oils or fats only will be used as adulterants that are lower in price than the oil or fat to be adulterated. Hence, it will greatly facilitate the examination of a totally unknown mixture of oils and fats to learn its price, for this alone will tend to exclude a number of more expensive substances from the scope of the analysis. In order to assist in fixing the attention on the oils lower in the scale of prices than the sample under examination, the following list, ranged in the order of the commercial value of oils, may be found useful. It should, however, be borne in mind that these prices are subject to wide fluctuations from year to year, causing, *e.g.* cotton seed oil and linseed oil to change places.

Oils and Liquid Waxes

1. Almond oil
2. Sperm oil
3. Olive oil
4. Neat's foot oil
5. Lard oil
6. Cod liver oil
7. Arctic sperm oil
8. Arachis oil
9. Poppy seed oil
10. Sesamé oil
11. Seal oil
12. Rape oil
13. Castor oil
14. Cotton seed oil—Maize (corn) oil
15. Linseed oil
16. Whale oil
17. Cod oil
18. Japan fish oil
19. Mineral oil
20. Rosin oil

Fats and Waxes

1. Cacao butter
2. Butter fat
3. Beeswax
4. Carnaüba wax
5. Chinese wax
6. Lard
7. Cocoa nut oil
8. Palm nut oil
9. Tallow
10. Paraffin wax
11. Palm oil
12. Bone fat

The object of technical analysis will be reached in the readiest possible manner by adopting a systematic plan, based broadly on the application of the general methods described in the preceding chapters.

If a known oil, fat, or wax be under examination, it will be advisable to first consult the description of that oil, fat, or wax, and especially the tables containing its characteristic numbers given in Chapter XIV. An endeavour will be made there to conclude the description of most of the individual oils and fats by pointing out those adulterants that fall within the range of practical consideration and the methods of detecting them. In short, each individual product will be considered as an analytical problem. It must, of course, be borne in mind that the commercial oils and fats vary with the climate and species of plant in the case of vegetable products, and, in the case of animal products, are influenced by the race of the animal as also by the mode of feeding. The following two examples will illustrate this point:—Some years ago olive oils having a higher iodine value than 85 or 87 would certainly have been considered as adulterated; yet Californian, Dalmatian, and Morocco olive oils of undoubted purity have been found to absorb more iodine. Therefore, olive oils can no longer be condemned on the strength of a high iodine value alone. Extremely instructive in the same respect are the commercial lards, especially those of American origin. Whereas a few years ago a lard having the iodine value of 63-65 would have raised the presumption of being adulterated, having

reached the limits which a genuine lard should show, yet pure lards are at present coming into the market possessing iodine values largely exceeding that limit. These lards must be allowed to pass muster, since the fattening of hogs (especially in the United States) on cotton cake and (or) corn (maize) produce "soft lards" in consequence of the vegetable oils passing into the body fat.

If it be borne in mind that adulteration has almost become a fine art, and that it is being carried out with the full armour of scientific knowledge by experts who are frequently some years ahead of the knowledge possessed by the analytical chemist, it will readily be understood that methods and tests must be selected and adapted to each special case by the analyst.

The plan followed in the description of general methods (chaps. v.-x.) will roughly indicate the succession of methods to be applied in the examination of a given sample. In the first instance it is advisable to derive the fullest information by testing the oils and fats themselves; after that the examination of the fatty acids may be attacked. In the following lines some typical examples will be considered.

Determination of Neutral Fat and Free Fatty Acids in a given Sample

This is a frequently occurring problem, *e.g.* when it is required to ascertain how far saponification of a neutral fat has proceeded in a technical saponification process. Let k, the saponification value of a sample of autoclaved tallow, be 203·0, and its acid value, $a = 162{\cdot}2$. Then the difference $k - a = 203{\cdot}0 - 162{\cdot}2 = 40{\cdot}8$ corresponds to the neutral fat present in the sample. Since the saponification value of neutral tallow is, in round figures, 195, we have the proportion:—

$$195 : 100 :: 40{\cdot}8 : x; \quad \text{hence } x = 20{\cdot}92.$$

The percentage of neutral fat in the sample is therefore 20·92, and the proportion of free fatty acids 100 − 20·92 = 79·08.

The fatty acids may also be determined gravimetrically, and this would become necessary in the case of a mixture of free fatty acids derived from one kind of fat, with a neutral fat of another kind. In that case several grams of the sample are weighed off accurately in a flask, hot alcohol and phenolphthalein are added, and the free fatty acids neutralised carefully by running in standard alkali until the solution just acquires a permanent pink colour. The liquid is allowed to cool, diluted with an equal volume of water, and shaken out in a separating funnel with ether or petroleum ether as described under the heading "Determination of the Unsaponifiable Matter." The aqueous layer is drawn off, and the ether layer repeatedly washed with water. The ethereal solution yields, after evaporation of the solvent, **the neutral fat.** From the aqueous layer the free fatty acids are separated by means of mineral acid, and their weight

may be determined as described under the heading "Hehner Value." Their mean molecular weight may then be determined, as also the mean molecular weight of the fatty acids in the neutral fat, after saponifying the latter and isolating the liberated fatty acids.

If the mean molecular weight of the free fatty acids were known from the outset, the quantity can be determined without weighing, by calculating their amount from the number of c.c. of normal potassium hydrate used in the neutralisation of the free fatty acids.

The next important step in the examination of a given sample is to determine the **iodine value**, and the results obtained thereby will in many cases permit to definitely establish the nature of the oil or fat. Simultaneously the state of freshness or rancidity may be ascertained, provided, of course, that no unsaponifiable matter be present. *If this be suspected, then the determination of the unsaponifiable matter may be combined with the determination of the* saponification value, as shown above (chap. vi.).

The following example may illustrate the foregoing remarks.

Edible Oil

yielding the following numbers on examination :—

Acid value	3·2
Saponification value . . .	196·1
Iodine value	109·3
Unsaponifiable	0·82 per cent

We conclude that the sample is practically a completely saponifiable oil, which cannot belong *to the rape oil group. Its iodine value points to cotton* seed oil. *From the acid value we calculate, on referring to the conversion table* (chap. vi. p. 279), that the sample contains 1·6 per cent of free fatty acids, taking 282 as their mean molecular weight, which differs very slightly from the actual mean molecular weight of cotton oil fatty acids given in the table (chap. viii. p. 334).

If a mixture of **two oils** is under examination, the nature of which is known, or can be readily identified, then it is possible to approximately calculate the proportion of both oils, provided their iodine values show sufficiently large differences. The following example may illustrate this.

Edible Oil

(sold as olive oil) gave on examination the following numbers :—

Acid value	3·2
Saponification value . . .	196·1
Unsaponifiable matter . . .	0·82 per cent
Iodine value	93

The iodine value being rather too high for olive oil, the presumption of adulteration is raised immediately. Oils of the rape oil class are excluded by the saponification value; the presence of almond oil is precluded by its higher price. Reference to the table of the iodine values (p. 253) would suggest the presence of either cotton seed oil or arachis oil. If the *Halphen* colour test (chap. xiv. "Cotton Seed Oil") has revealed the presence of cotton seed oil, we may calculate the proportion of it in the sample by the following two equations. Let x be the percentage of olive oil and y the percentage of cotton seed oil, then we have $x + y = 100$. Taking the mean iodine values of olive oil and cotton seed oils as 85 and 109 respectively, we obtain the second equation

$$\frac{85x}{100} + \frac{109y}{100} = 93. \quad \text{Hence } x = 66{\cdot}6 \text{ per cent.}$$

If the *Halphen* test for cotton seed oil has been negative, the sample must be examined for the presence of arachidic acid, and the calculation therefrom to arachis oil will furnish the approximate percentage of the proportion of arachis oil. The calculation of the constituents from the iodine values, as above, would obviously lead to very uncertain results.

If the saponification value of a sample has directed attention to the presence of **soluble fatty acids,** then the Reichert value, as also sometimes the determination of the Hehner value (in absence of considerable amounts of unsaponifiable matter) will be of material assistance. This may be best illustrated by the calculation of the approximate composition of a sample of

Butter Fat

The following numbers were determined :—

Acid value	0·56
Reichert-Meissl value	28·1
Hehner value	87·5
Iodine value	32·6
Mean molecular weight of the insoluble fatty acids .	260
Stearic acid in the insoluble fatty acids . .	0·49 per cent.

From the low acid value the conclusion is drawn that mono- and diglycerides are practically absent.

From the mean molecular weight of the insoluble fatty acids 260, the mean molecular weight of the corresponding glycerides is calculated as $3 \times 260 + (C_3H_3)38 = 818$. The percentage of glycerides of insoluble fatty acids is therefore 91·8 per cent as calculated from the following proportion :—

$$(3 \times 260) : 818 = 87{\cdot}5 : x \,; \quad x = 91{\cdot}8 \text{ per cent.}$$

The glycerides of insoluble fatty acids consist of laurin, myristin, palmitin, stearin, traces of arachin, and olein (linolin being assumed to be absent).

The iodine value of 32·6 leads to the percentage of olein = 38·02 by the following calculation :—

$$86\cdot2 : 100 = 32\cdot6 : x ; \quad x = 38\cdot02.$$

The amount of stearic acid in the insoluble fatty acids was found = 0·49 per cent, corresponding to 0·51 per cent stearin [(3 × 284) : 890 : : 0·49 : x]. This corresponds to 0·46 per cent stearin in the butter fat. Since the glycerides of volatile fatty acids make up the difference, the composition of the butter fat under examination may be preliminarily taken to be as follows :—

Stearin	0·46 per cent
Laurin, myristin, palmitin, arachin[1]	52·38 ,, ,,
Olein	38·02 ,, ,,
Butyrin, caproin, etc. (by difference)	9·14 ,, ,,
	100·00

A further insight into the nature of the volatile acids may be gained from the amount of potassium hydrate required to saturate the total volatile fatty acids obtained by the process described on p. 342. The experiment gave 41·4 mgrms. potassium hydrate (the value corresponding to the above-given Reichert-Meissl value is 31·47) per gram of butter fat. The volatile acids from 100 grms. of butter fat would therefore require 4·14 grms. KOH. The mean molecular weight of the volatile fatty acids could be calculated if their absolute weight were known. This can be derived from the weight of their glycerides found above (by difference) as 9·14 per cent. Since 3 × 56·1 = 168·3 potassium hydrate correspond to 92 parts of glycerol (in the absence of mono- and diglycerides), or to 38 parts C_3H_2, the 4·14 grms. KOH correspond to

$$\frac{38 \times 4\cdot14}{168\cdot3} = 0\cdot93 \text{ grms. } C_3H_2.$$

The percentage of the volatile fatty acids in the sample is therefore 9·14 − 0·93 = 8·21. Since 8·21 grms. of the mixed volatile acids required 4·14 grms. of KOH, their mean molecular weight must be

$$M : 56\cdot1 : : 8\cdot21 : 4\cdot14. \quad M = 112.$$

From the following table it must be concluded that lauric and capric acids can only be present in very small quantities amongst the volatilised acids, whereas butyric and caproic acids preponderate :—

[1] Cp. the composition of the solid fatty acids as given by Partheil and Ferié, chap. xiv. "Butter Fat."

Acid.	Formula.	Molecular Weight Theory.
Butyric . .	$C_4H_8O_2$	88
Caproic . .	$C_6H_{12}O_2$	116
Caprylic . .	$C_8H_{16}O_2$	144
Capric . .	$C_{10}H_{20}O_2$	172
Lauric . .	$C_{12}H_{24}O_2$	200

Further information with regard to the composition of the glycerides of volatile acids will be given under "Butter Fat" (chap. xiv.).

In more complicated cases, such as are presented by a mixture of *three oils or fats, the examination of the* **mixed fatty acids** *becomes* imperative. The first indications will be obtained by the determination of the melting and solidifying points of the mixed fatty acids *and their mean molecular weights. Next their iodine value will be* determined. I have endeavoured in Chapter VIII. to indicate a systematic course of examining the mixed fatty acids, the reader must *therefore be referred to p. 331. It will only be required to supple*ment the directions given there by some additional explanations.

In the first instance, separation of the solid from the liquid fatty acids will be resorted to, and the amount of unsaturated fatty acids contained in the former determined by the iodine value. In most cases it will be accurate enough to calculate to oleic acid, and correct accordingly the mean molecular weight of the saturated fatty acids.

If stearic acid be present, it should be determined in a direct manner. If a mixture of two acids of known composition be under examination, their respective proportions may be derived approximately by calculation from the mean molecular weight of the mixed acids, provided that this number has been determined with great accuracy.

The mean molecular weight of the mixed fatty acids, M, should be determined with not less than 5 grms. of substance. Then, letting x and y be the percentages, and M_1 and M_2 the molecular weights of the fatty acids respectively, then x and y can be calculated from the following equations :—

$$x + y = 100,$$

$$\frac{M_1 x}{100} + \frac{M_2 y}{100} = M.$$

For practical purposes, as in a works where mixtures of known fatty acids are examined frequently, it is advisable to construct a table such as the following, calculated by *Mangold*, for stearic and palmitic acids :—

[TABLE

Mixed Stearic and Palmitic Acids

Neutralisation Value. Mgrms. of KOH per 1 grm.	Mean Molecular Weight.	100 parts of the mixture contain	
		Stearic Acid.	Palmitic Acid.
197·5	284	100	—
198·5	282·6	95	5
199·5	281·2	90	10
200·5	279·8	85	15
201·5	278·4	80	20
202·5	277·0	75	25
203·5	275·6	70	30
204·6	274·2	65	35
205·6	272·8	60	40
206·7	271·4	55	45
207·77	270·0	50	50
208·86	268·6	45	55
209·95	267·2	40	60
211·06	265·8	35	65
212·18	264·4	30	70
213·30	263·0	25	75
214·45	261·6	20	80
215·60	260·2	15	85
216·77	258·8	10	90
217·95	257·4	5	95
219·13	256·0	—	100

The examination of the **liquid fatty acids** is a more complicated problem, and in the present state of our knowledge the examination will, in the first instance, be confined to the qualitative detection of oleic, linolic, and linolenic acids. If oleic, linolic, and linolenic acids have been detected qualitatively,[1] then it is possible to approximately calculate their proportions from the mean molecular weight of the liquid fatty acids and their iodine value, both numbers having been found by direct determinations. Let M be the molecular weight of the mixed liquid fatty acids, M′ the molecular weight of oleic acid (282), M″ the molecular weight of linolic acid (280), and M‴ the molecular weight of linolenic acid (278). Further, let I be the iodine value of the mixed liquid fatty acids, I′ the iodine value of oleic acid (90·07), I″ the iodine value of linolic acid (181·42), and I‴ the iodine value of linolenic acid (274·1). Then the percentages of x, y, and z of the three acids may be calculated from the following three equations:—

$$x + y + z = 100,$$
$$I'x + I''y + I'''z = 100\ I,$$
$$M'x + M''y + M'''z = 100\ M.$$

It must, however, be distinctly understood that these calculations should only be looked upon as furnishing rough approximations, and

[1] Oleic acid by means of its oxidation product dihydroxystearic acid. Cp. however, "Linseed Oil," chap. xiv.

should only be employed if no other method is available. At best they should only be used to confirm results obtained by quantitative methods.

For the examination of the **unsaponifiable matter** it is necessary to isolate a quantity sufficient to perform the tests described in Chapter IX. One of the most important operations under this head is the **phytosteryl acetate test,** whenever the question of the

Detection of Vegetable Oils and Fats in Oils and Fats of Animal Origin

is raised. This test is very important in the examination of lard, when a high iodine value raises the presumption of adulteration with cotton seed oil, and this presumption has been corroborated by a positive Halphen test (see chap. xiv. "Lard.")

The converse problem of detecting small quantities of animal oils in vegetable oils (as *e.g.* lard oil in olive oil[1]) is at present still awaiting solution.

The *modus operandi* to be adopted in the case of products containing large amounts of unsaponifiable matter may be explained by the examples of "recovered grease" and "distilled grease."

"Recovered Grease"[2]

(Crude Wool Fat)

The determination of the following constituents of recovered grease would be required (cp. chap. xv.):—

(*a*) Free fatty acids.
(*b*) Neutral fat.
(*c*) Unsaponifiable matter.

(*a*) *Free Fatty Acids*

The amount of alkali required to saturate the free fatty acids in 1 grm. of the "recovered grease" was 0·71 c.c. normal KOH (acid value = 39·8). A large weighed quantity of "recovered grease" was then nearly neutralised with the greater part of the alkali required, as calculated from the acid value, and then carefully titrated with half-normal alkali, until the solution became pink to phenolphthalein. A large proportion of neutral fat and unsaponifiable matter rose to the top as an oily layer, and was separated from the soap solution,

[1] Cp. *Journ. Soc. Chem. Ind.* 1903, 1153.
[2] Lewkowitsch, *Journ. Soc. Chem. Ind.* 1892, 134; cp. also *ibid.* 1896, 14.

after having been dissolved in ether. The remainder of the neutral fat and unsaponifiable matter was removed from the soap solution by shaking out with ether. The ethereal solutions were united, freed from adhering soap by washing with water, and the solvent was then distilled off. Thus the neutral fat (*b*) and the unsaponifiable matter (*c*) were obtained together.

Between the aqueous and the ethereal layers there appeared a flocculent stratum, which was found to consist of an insoluble soap. It was isolated by filtering off from the soap solution. The fatty acids of both the soap solution and the insoluble soap were separated in the usual manner by decomposing with a mineral acid. Thus the *free fatty acids* of the "recovered grease" were obtained in two *fractions, viz.* (1) *acids, forming soluble soaps*; (2) *acids, forming insoluble soaps.*

Both kinds of acids were found to contain inner anhydrides or lactones (increase of weight on boiling with acetic anhydride, cp. p. 289); for the determination of the molecular weight the acids had therefore to be boiled with standardised alcoholic potash. The molecular weights were found to be respectively 326 and 520. The proportion of the acids (1) to the acids (2) being 9 : 1, the mean molecular weight of *all* free fatty acids may be taken as—

$$\frac{9 \times 326 + 520}{10} = 345.$$

The *Reichert-Meissl* value of the recovered grease was 6·2, or, in other words, 1 grm. required 0·124 c.c. normal potash for neutralisation of the volatile fatty acids. Assuming as their mean molecular weight 102 ($C_5H_{10}O_2$), the "recovered grease" contains $10·2 \times 0·124 = 1·26$ per cent of *volatile acids.*

The insoluble free fatty acids in 1 grm. were saturated by $0·71 - 0·124$ c.c. $= 0·586$ c.c. normal potash. Their mean molecular weight being 345, we find $34·5 \times 0·586 = 20·22$ per cent of *insoluble free fatty acids.*

(*b*) and (*c*) *Neutral Fat and Unsaponifiable Matter*

A somewhat large quantity of the substance (*b*) and (*c*), prepared as already described, was saponified, and the soap solution tested for *glycerol.* The negative result proved *absence of glycerides.* The neutral fat must, therefore, be considered a *wax.*

The ether residue obtained by extracting the saponified mass with ether, and evaporating off the latter, was completely dissolved by acetic anhydride, no oily layer separating on cooling (p. 377). Therefore, *hydrocarbons* were absent, and the *unsaponifiable matter* (*c*) could only consist of alcohols.

The wax (*b*) was separated from the unsaponifiable matter (*c*) by judicious boiling out with alcohol,[1] in which the wax is almost

[1] Preferably acetic anhydride.

insoluble. The latter was thus obtained as a viscous, wax-like substance, melting into a thick liquid at about 40° C.

On saponification with double normal alcoholic potash under pressure (p. 61), 1 grm. of the wax was found to require 1·825 c.c. of normal potash, or, in other words, its saponification value was 102·4.

The alcohols (*unsaponifiable*) were determined in the usual manner by extracting the saponified mass with ether; the fatty acids were then estimated in the soap solution by *Hehner's* method. Thus the composition of the wax was found in two analyses as follows:—

	I.	II.
	Per cent.	Per cent.
Fatty acids	56·3	54·1
Alcohols	43·2	44·0
	99·5	98·1

The sum of the constituents of the wax should have been higher than 100, several per cents of water being assimilated on saponification. The deficiency must be looked for in the number obtained for the fatty acids, this having been found too low, owing to the property of these acids of easily losing water on drying, with formation of inner anhydrides or lactones. The molecular weight of these fatty acids was found to be 327·5 when using *alcoholic* potash for the determination, wherefrom the percentage composition of the wax may be calculated as follows:—

	Per cent.
Fatty acids, 1·825 × 32·75 = ...	59·77
Alcohols (mean of values in analyses I. and II.) .	43·60
	103·37

The *mean molecular weight of the alcohols* calculated from the equation

$$M = \frac{43 \cdot 6 \times 327 \cdot 5}{59 \cdot 77}$$

was found to be 239.

The fatty acids absorbed only 17 per cent of *iodine*; they consist, therefore, for the most part of saturated acids.

(*c*) *Unsaponifiable Matter*

The proportion of unsaponifiable matter was found *approximately* by analysing the mixture of (*b*) and (*c*) in the same manner as (*b*), and comparing the numbers obtained as follows:—

1 grm. of the mixture of (*b*) and (*c*) required 1·73 c.c. of normal

KOH on saponification. Its percentage composition was found as follows:—

	I. Per cent.	II. Per cent.
Fatty acids	50·7	49·8
Alcohols	47·5	47·6
	98·2	97·4

From these numbers we calculate—

	Per cent.
Fatty acids, 1·73 × 32·75	56·66
Alcohols	47·55
	104·21

The 56·66 parts of fatty acids require 41·34 per cent of alcohols, mean molecular weight 239, to form wax. Consequently there are present in the "recovered grease" 47·55 − 41·34 = 6·21 per cent of *unsaponifiable matter*.

The composition of the "recovered grease" is therefore—

	Per cent.
Volatile fatty acids	1·26
Insoluble free fatty acids	20·22
Unsaponifiable matter (uncombined alcohols)	6·21
Wax (wool wax) by difference	72·31
	100·00

To check the result, the sum of the alcohols and of the wax could have been determined direct.

The number 72·31 for wax can be resolved, with the help of its above-given percentage composition (fatty acids, 59·77 per cent; alcohols, 43·60 per cent), into two numbers expressing its component parts, viz. 72·31 × 0·5977 = 41·81 per cent of fatty acids, and 72·31 × 0·436 = 30·5 per cent of alcohols. The total unsaponifiable matter obtainable from the "recovered grease" on complete saponification is, therefore, 30·5 + 6·21 = 36·71 per cent. Hence we express the analytical result as follows:—

		Per cent.	
	Volatile fatty acids	1·26	
	Insoluble free fatty acids	20·22	
	Unsaponifiable matter (uncombined alcohols)	6·21	Total unsaponifiable Matter. 36·71
Wax	Combined alcohols	30·50	
	Combined fatty acids	41·81	

The percentage of the *total unsaponifiable matter*—36·71—can, of course, be verified by direct determination, which can be suitably combined with that of the saponification value. Direct experiment gave the number 36·47 (see below).

A more rapid, and for technical purposes sufficiently accurate, method would be to determine the *acid value*, the *saponification value*, the proportion of *total unsaponifiable matter*, the *mean molecular weight of the total insoluble acids*,[1] and, if required, the *Reichert-Meissl value*. The following numbers were thus obtained :—

1 grm. required for the neutralisation of the volatile acids	.	0·124 c.c. of normal KOH
1 ,, ,, ,, ,, ,, free insoluble acids		0·586 c.c. ,, ,,
1 ,, ,, ,, ,, ,, total insoluble acids	.	2·19 c.c. ,, ,,
1 ,, ,, ,, ,, ,, combined insoluble acids (by difference)		1·48 c.c. ,, ,,
Mean molecular weight of the total insoluble acids	.	332[2]
Unsaponifiable matter	.	36·47 per cent.

From these analytical data we obtain :—The percentage of the free insoluble acids, $0·586 \times 33·2 = 19·45$; the percentage of the combined fatty acids, as hydrated acids, $1·48 \times 33·2 = 49·13$; and the percentage of volatile acids, $0·124 \times 10·2 = 1·26$ as before.

In the following table these numbers are collated :—

	Per cent.
Volatile fatty acids	1·26
Insoluble free fatty acids	19·45
Combined fatty acids (as hydrated acids)	49·13
Total unsaponifiable matter	36·47
	106·31

Part of the surplus over 100 is due to the proportion of water assimilated on saponification; the remainder is due to an error in the number found for the molecular weight of the total insoluble fatty acids, caused by the difficulty of titrating accurately the dark alcoholic solutions.

It would not have been permissible to determine the *proportion* of the total fatty acids by *Hehner's* method, the result obviously coming out too low owing to the formation of inner anhydrides.

"Distilled Grease"[3]

(*Liquid Portion*)

The liquid portion of the distillate obtained on a large scale by subjecting the "recovered grease" to distillation gave on examination the following results :—

[1] This must be determined with *alcoholic* potash (cp. above).

[2] This number is somewhat too high, owing to the dark colour of the alcoholic solution of the fatty acids.

[3] Lewkowitsch, *Journ. Soc. Chem. Ind.* 1892, 141.

(*a*) 1 grm. required for the neutralisation of the free fatty acids	1·92 c.c. of normal KOH
(*b*) 1 grm. required for the neutralisation of the total fatty acids on saponification	2·10 c.c. ,, ,,
(*c*) 1 grm. required therefore for the neutralisation of the combined fatty acids	0·18 c.c. ,, ,,
(*d*) Mean molecular weight of the total fatty acids[1]	300·5
(*e*) Total unsaponifiable matter	38·8 per cent.

From the numbers recorded under (*c*) and (*d*) and (*e*) the composition of the distilled grease may be expressed thus :—

	Per cent.
Fatty acids (as hydrated acids), 2·1 × 30·05	63·1
Total unsaponifiable matter	38·8
	101·9

The low number obtained for the combined fatty acids shows that the greater portion of the wax had been decomposed during distillation.

The free fatty acids were isolated as described p. 411; their mean molecular weight was 286; they may, therefore, be considered as consisting of a mixture of oleic, stearic, and palmitic acids, with a small proportion of higher fatty acids. The proportion of free fatty acids in the "distilled grease" was, therefore, 1·02 × 28·6 = 54·91 per cent.

The wax *plus* the unsaponifiable matter was isolated in the same manner as described p. 410. The separation of these two constituents was, however, impossible, the unsaponifiable matter being also insoluble in alcohol. The mixture of the two substances was therefore saponified, so as to isolate the fatty acids contained in the wax. They were found to have the molecular weight 394, as determined by means of *alcoholic* potash. The proportion of combined fatty acids in the "distilled grease" was, therefore (2·10 - 1·92) × 39·4 = 7·09 per cent.

The alcohol combined with the latter acids was contained in the total unsaponifiable matter. Its presence was proved, on the one hand, by boiling an accurately weighed portion with acetic anhydride, and ascertaining that an increase in weight had taken place; and, on the other hand, by isolating the alcohol from the total unsaponifiable matter by means of alcohol.

Adopting the molecular weight for the alcohols that had been found (p. 411) for the combined alcohols in the "recovered grease," we can calculate the proportion of *alcohols* from the equation

$$x = \frac{7 \cdot 09 \times 239}{394};$$

hence $x = 4 \cdot 3$.

The amount of *undecomposed wax* in the "distilled grease" is,

[1] Determined with *alcoholic* potash.

therefore, neglecting the small amount of water assimilated on saponification, 7·09 + 4·3 = 11·39 per cent.

The remainder of the unsaponifiable matter, 38·8 − 4·3 = 34·5 per cent, consists of hydrocarbons formed in consequence of the free fatty acids and of the wax of the "recovered grease" having been decomposed during distillation.

The composition of the "distilled grease" is expressed by the following numbers :—

	Per cent.	
Free fatty acids	54·91	
Combined fatty acids	7·09	Undecomposed Wax. 11·39
Combined alcohols	4·30	
Unsaponifiable matter (hydrocarbons)	34·50	
	100·80	

CHAPTER XII

EXAMINATION BY STRICTLY SCIENTIFIC METHODS

In case the information obtained by the methods described in the foregoing chapters is not deemed sufficient for the elucidation of the composition of a given product, recourse must be had to strictly scientific methods. These do not fall, as a rule, within the province of the technical analysis of oils, fats, and waxes.

The methods to be employed in a research of this kind would embrace :—fractional crystallisation of the original oils and fats, and after saponification has been effected, fractional distillation and fractional precipitation of the fatty acids. Similar methods would suggest themselves for the examination of the unsaponifiable matter of the waxes. Many of the analytical processes described in the foregoing chapters have passed through the stage of a strictly scientific research, before they were worked out so as to constitute an expeditious technical method. *Since it may not infrequently become necessary to undertake further research, I collate in this chapter a number of methods which at present may be termed strictly scientific.* It may *also prove useful to record here some proposed methods that have not led as yet to useful results, but may offer hints and suggestions for further elaboration.*

A. Examination of the Glycerides

(*a*) *Fractional Crystallisation of Glycerides*

It has been pointed out already that the oils and fats are more or less complicated mixtures of several triglycerides and that recent researches have shown (chap. i.) that the occurrence of mixed triglycerides must be more frequently taken into account than has been done hitherto. The mixed glycerides described (chap. i.) have been isolated by fractional crystallisation. Not until a well-crystallised substance has been obtained, will ultimate (elementary) analysis furnish any useful indications, as will be seen by glancing at the following table, stating the percentages of carbon, hydrogen, and oxygen contained in palmitin, stearin, olein, linolin, ricinolein, and

in a number of commercial oils and fats which were examined by earlier observers.

Triglyceride.	Formula.	Carbon. Per cent.	Hydrogen. Per cent.	Oxygen. Per cent.
Palmitin . . .	$C_{51}H_{98}O_6$	75·93	12·16	11·91
Stearin . . .	$C_{57}H_{110}O_6$	76·85	12·36	10·79
Olein . . .	$C_{57}H_{104}O_6$	77·38	11·76	10·86
Linolin . . .	$C_{57}H_{98}O_6$	77·90	11·16	10·94
Ricinolein . .	$C_{57}H_{104}O_9$	73·39	11·16	15·45

Kind of Fat.	Carbon. Per cent.	Hydrogen. Per cent.	Oxygen. Per cent.
Linseed oil [1]	76·80	11·20	12·00
,, ,, ...	77·80	11·20	11·80
,, ,, ...	78·00	11·00	11·00
Rape oil [1]	77·99	12·03	9·98
,, ,, ...	78·20	12·08	9·72
,, ,, ...	77·91	12·02	10·07
Finback oil [2]	77·05	12·05	10·90
Train oil [2]	76·85	11·80	11·35
Cod liver oil [2]	75·91	12·22	11·87
Seal oil [2]	77·10	13·50	9·40
Horse fat [1]	77·07	11·69	11·24
Lard [1]	76·54	11·94	11·52
Beef tallow [1]	76·50	11·91	11·59
Mutton tallow [1]	76·61	12·03	11·36
Butter fat [1]	75·63	11·87	12·50

The earlier experiments undertaken by *Heintz* to obtain pure stearin from tallow by repeated crystallisation from ether did not lead to chemically pure substances, but the method employed by him has recently been taken up with greater success, and a number of mixed glycerides (described in chap. i.) have been prepared. The first mixed glyceride was obtained by precipitating the ethereal solution of mkányi fat by alcohol (*Heise*). *Holde*[3] in an investigation of olive oil cooled the ethereal solution to − 40 to − 45° C. Another method employed for the resolution of the glycerides is based on the crystallisation from a mixture of chloroform and ether (*Fritzweiler*) or acetone (*Klimont*). *Kreis* and *Hafner*,[4] however, have shown that by mere crystallisation from alcohol, ether, benzene, and amyl alcohol it is not possible to obtain glycerides free from olein or mixed glycerides containing oleic acid. The latter so tenaciously adheres to the glycerides that although the recrystalled glyceride retains its melting point unaltered, it still absorbs iodine. The impurity can, however, be removed by treating the glyceride with *Hübl* solution,

[1] Schulze and Reinecke; Liebig's *Annalen*, 142. 198; König, *Chemische Zusammensetzung der Nahrungsmittel*, etc., i. 199, 200, 420.
[2] Schaedler, *Technologie der Fette und Oele*, 750.
[3] *Berichte*, 1901, 2402. [4] *Ibid.* 1903, 1126.

so as to convert the oleo-glyceride into its chloro-iodo-compound. The latter can then be more readily removed by crystallisation from benzene or alcohol, and finally from ether.

The foregoing methods appear to be full of promise for the successful resolution of the mixtures of glycerides, with which we have to deal in the ordinary oils and fats. Hitherto, however, hardly more than a beginning has been made.

(b) *Fractional Distillation of Glycerides*

The glycerides of the lower fatty acids can be fractionally distilled in complete vacuum without undergoing decomposition. *Krafft*[1] has shown that higher glycerides than those of lauric and myristic acids can no longer be obtained by this method. Thus by distilling laurel oil and nutmeg butter *in vacuo*, laurin and myristin were found in the distillate practically undecomposed, so that by recrystallisation the pure glycerides could be prepared. On subjecting Japan wax to the same process, dipalmitin underwent decomposition.

B. Examination of the Fatty Acids

The process described in Chapter VIII. permits to distil off all the volatile acids contained in the commercial oils and fats, and thus to separate them almost completely from the insoluble acids.

(a) *Examination of the Volatile Fatty Acids*

In the table (p. 343) the amount of potassium hydrate required to saturate the total volatile acids in a number of oils and fats has been given. The neutralised distillate is then boiled down to a small volume and the bulk of the volatile acids is liberated as an oily layer by adding to the solution of the potassium salts fairly concentrated sulphuric acid. The aqueous acid layer may again be subjected to distillation in order to recover the last traces of the most volatile acids or may be extracted with ether.

According to *Liebig*, the aqueous solution of the volatile fatty acids is divided into two equal parts. One part is neutralised exactly by caustic potash ; the second part is then added, and the whole subjected to distillation. The acids having low boiling points pass into the distillate, whilst the higher boiling acids remain as potassium salts in the distilling flask. Acetic acid, however, if present, also remains behind as potassium salt. By repeatedly treating both the distilled and the remaining acids in the same way, finally pure fractions of the several acids are obtained.

[1] *Berichte*, 1904, 4842.

Liebig employed this method for separating butyric acid from a mixture of butyric and isovaleric acids, and further for isolating acetic acid when mixed with either of these two acids. *Veiel*, however, arrived at the opposite result, having found that isovaleric acid distilled over, whereas butyric acid remained behind. *Lieben* partially confirmed *Veiel's* results, by stating that *Liebig's* method is not accurate. He obtained, however, approximately satisfactory separation by suitably modifying it, viz. by partially neutralising the mixture of acids, the higher acids could be distilled off whilst the lower remain behind as salts. *Wechsler*[1] applied *Lieben's* method to equivalent amounts of two acids; he examined the following mixtures: formic and acetic, acetic and propionic, acetic and butyric, acetic and isobutyric, propionic and butyric, butyric and caproic acids. The mixed acids were neutralised with four-fifths of the theoretical amount of alkali, and distilled so long as the distillate was found to be acid. The remaining salts were then treated with a quantity of sulphuric acid required to exactly liberate three-fifths of the fatty acids, and again distilled. The last fifth was finally obtained by acidulating the residue and distilling it. The first fraction was found to contain the higher acid, and the last fraction the lower acid, in an almost pure state. The mixture of butyric and isovaleric acids, however, could not be separated by this method, a result at variance with the statements of both *Liebig* and *Veiel*. *Crossley*,[2] again, could not obtain such good results as one is led to expect from *Wechsler's* statements, and in his opinion the latter's method cannot in any way be looked upon as a satisfactory one for separating mixtures of fatty acids. On distilling fermented wool-scouring liquors, *A.* and *P. Buisine*[3] found that of the volatile fatty acids those with a higher number of carbon atoms distilled over first.

Erlenmeyer and *Hell*[4] propose to separate the several volatile acids by fractional saturation with silver carbonate. The acids having a higher boiling point are precipitated first.

Fitz[5] has shown that by mere fractional distillation of the free acids, if care is taken to replace the water distilled off, a separation can be effected, the acid of higher molecular weight passing over first. This result has been corroborated by *Hecht*[6] (cp. also chap. iii.[7]).

(*b*) *Examination of the Non-Volatile Fatty Acids*

The non-volatile acids can be separated into *solid* (saturated) and *liquid* (unsaturated) acids by exhausting their lead salts with ether (see p. 347).

[1] *Journ. Soc. Chem. Ind.* 1894, 179; cp. also Sorel, *ibid.* 1896, 15 (543), 143.
[2] *Proc. Chem. Soc.* 1897, 21.
[3] *Chem. Centr.* 1898, 23.
[4] Liebig's *Annalen*, 160. 296, footnote.
[5] *Berichte*, 11. 46.
[6] Liebig's *Annalen*, 209. 319.
[7] For further information the reader may be referred to papers by Duclaux (*Ann. Phys. Chim.* [5] 2, 289 (1874)); Haberland (*Zeit. anal. Chem.* 1899, 217); Chapman (*Analyst*, 1899, 114); Holzmann (*Arch. d. Pharm.* 1898, 409); Muspratt (*Journ. Soc. Chem. Ind.* 1900, 207); Crossley (*Journ. Chem. Soc.* 1897, 580).

The separation by means of the lead-salt-ether method is not a quantitative one, as has been pointed out already (p. 348). It is likely that by repeating the extraction of the lead salts in which the saturated acids preponderate, one may arrive in some cases at lead salts free from unsaturated acids. Yet in the case of a specimen of linseed oil fatty acids examined in my laboratory, the fatty acids of the insoluble lead salts had the iodine value 22·34, and formed 8·9 per cent of the total fatty acids. After passing the solid fatty acids for a second time through the lead-salts-ether process, 7·5 per cent of solid acids were obtained, still absorbing 19·2 per cent of iodine.

Experiments made by the writer with a view to removing the unsaturated acids by converting them into chloro-iodo-compounds have not yet led to satisfactory results.

The **solid** saturated acids may be further separated by fractional precipitation of their alcoholic solutions (saturated in the cold) with alcoholic solutions of barium or magnesium acetate.[1] *Pebal*[2] uses as a precipitant an alcoholic solution of lead acetate. Every fraction is decomposed by hydrochloric acid, and the fatty acids of the same melting point are united. The several fractions are repeatedly subjected to the same process until pure substances are obtained. A fraction may only then be looked upon as a chemical individual if its melting point is not altered by further recrystallisation, and if by partial precipitation fractions having identical melting points are obtained.

It is thus evident that pure acids can only be obtained by a very frequent repetition of the fractional precipitation, and that quantitative isolation of the individual acids is altogether out of the question.

Experiments made by *Hehner* and *Mitchell*[3] on mixtures of palmitic and stearic acids with a view to determine the usefulness of such methods for analytical purposes, give an approximate idea as to how far separation may be effected. Pure stearic and palmitic acids were mixed in the proportions given in the following table, and precipitated with measured quantities of aqueous barium acetate solution sufficient to precipitate the stated amounts of stearic acid.

Separation effected by Precipitation of mixed Stearic and Palmitic Acids with Aqueous Barium Acetate

Stearic Acid. Grms.	Palmitic Acid. Grms.	Barium Acetate added sufficient to precipitate Stearic Acid. Grms.	Stearic Acid in Precipitate. Per cent.
1	1	1	71·7
1	2	1	62·8
1	3	1	27·9
1	3	1	30·9
0·5	0·5	0·5	62·7
1	1	0·5	46·6

[1] Heintz, *Journ. prakt. Chemie*, 66. 1.
[2] *Annalen*, 91. 138.
[3] *Analyst*, 1896. 318.

On precipitating the filtrates in a similar fashion, it not infrequently happened that the second fraction contained a larger proportion of stearic acid than the first fraction.

Similar experiments with aqueous solution of magnesium acetate and alcoholic solutions of lead acetate gave no better results.

Kreis and *Hafner*[1] suggest to determine in a mixture of stearic and palmitic acids, first, the amount of stearic acid as described (p. 355). They then dissolve the mixed fatty acids in so much alcohol that on cooling to 0° the palmitic acid (the amount of which was found by difference) remains in solution. After twelve to fourteen hours' standing in an ice-chest, they filter off and recrystallise the residue on the filter twice from alcohol; this is then looked upon

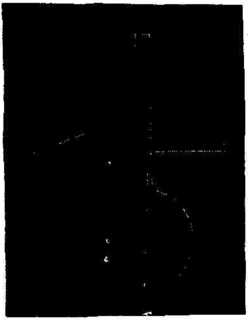


Fig. 52.

as pure stearic acid. The filtrate, which only contains 0·12 grms. of stearic acid per 100 c.c., is evaporated down to half its volume, and mixed with so much of an alcoholic magnesium acetate solution as is required for separating the dissolved stearic acid. After standing for twelve to fourteen hours at the ordinary temperature the precipitate is filtered off and the fatty acids recovered from the filtrate. Thus *Kreis* and *Hafner* found the melting point of the fatty acid at 60°. The acid is then dissolved in so much alcohol that it does not crystallise out at the ordinary temperature, and one-third of the previously used amount of magnesium acetate is then added. After repeating this operation once more and recrystallising from alcohol, pure palmitic acid of the melting point 62·3° was obtained. *Kreis* and *Hafner* are of the opinion that this process, in which the bulk of stearic acid is removed at the outset by simple crystallisation, is more expeditious than *Heintz's* method.

[1] *Berichte*, 1903, 2766

The separation of the liquid fatty acids by means of fractional distillation *in vacuo* has been resorted to by *F. Krafft.*[1] More recently *Krafft*[2] uses the vacuum of the cathode light; so high a vacuum, for the measurement of which the reading of a mercury gauge is useless, can be obtained without difficulty by employment of a *Babo* vacuum pump. The boiling points of fatty acids recorded in Chapter III. have been determined by means of this apparatus.

The somewhat complicated apparatus described by *Krafft* may be advantageously replaced in a technical laboratory by a combination of the two apparatus (Figs. 52 and 53), designed by the writer[3] for fractional distillation *in vacuo*, and found very convenient in daily use. It may be recommended for laboratories having a vacuum pipe provided with several taps.

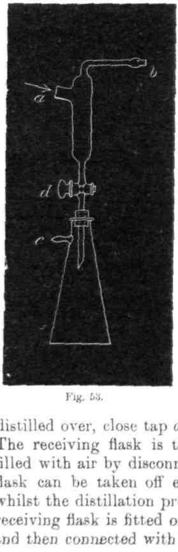


Fig. 53.

A finely-drawn tube fitted is soldered in the distilling flask. The tube is fitted on its outer end with an india-rubber tube and a screw-clamp, by means of which a current of air or indifferent gas can be drawn in, and at the same time the pressure regulated accurately. By means of this contrivance it is also feasible to prevent frothing of the liquid. Nozzle *a* of the adapter (Fig. 53) is connected with a *Liebig* condenser, and *b* and *c* by means of strong india-rubber tubing with two taps of a vacuum pipe. On starting the distillation, the distilling flask, the adapter, and the conical receiving flask are exhausted through *b* and *c*, the stopcock *d* being open. When the first fraction has distilled over, close tap *d* and then the vacuum tap connected with *c*. The receiving flask is thus shut off from the vacuum pipe, and is filled with air by disconnecting the india-rubber tubing from *c*. The flask can be taken off easily and emptied, or replaced by another, whilst the distillation proceeds without any interruption. When the receiving flask is fitted on again it is exhausted through *c*, as before, and then connected with the distilling flask by opening tap *d*.

More promising than the fractional distillation of the fatty acids would appear the fractional distillation of their methylic and ethylic esters. Experiments in this direction have not been carried out yet.

For the detection and examination of the highly unsaturated fatty acids in cod liver oil, *Bull*[4] proposed fractional crystallisation

[1] *Journ. Chem. Soc.* 1889, Abstr. 690.
[2] *Berichte*, 1896, 1316.
[3] *Journ. Chem. Soc.* 1889, Trans. 360.
[4] *Chem. Zeit.* 1899, 996; 1043.

of their sodium and potassium salts from alcohol and ether. He thus obtained fatty acids, the high iodine values of which (322 and 347) point to acids belonging to the series $C_nH_{2n-8}O_2$ (cp. "Cod Liver Oil," chap. xiv.). For further information the reader must refer to the original, since *Bull* himself contradicts and throws doubts on some of his own results.[1]

C. Examination of the Insoluble Alcohols

If a mixture of alcohols has been obtained, the isolation of the individual alcohols may be effected by fractional crystallisation. It will be found useful to convert the alcohols into their benzoic or acetic esters; the latter are easier to distil than the original substances, and can therefore be more effectively resolved into fractions cp. also (p. 377).

[1] *Chem. Zeit.* 1900, 814.

APPENDIX

PAGE 4

ON boiling the monoglycerides and diglycerides with acetic anhydride, triglycerides of the formulæ

$$C_3H_5O \cdot C_2H_3O \begin{cases} O \cdot R \\ \\ O \cdot C_2H_3O \end{cases}$$

and

$$C_3H_5O \cdot R \begin{cases} O \cdot R \\ \\ O \cdot C_2H_3O \end{cases}$$

are obtained. Similarly, on heating the mono- and diglycerides with benzoyl chloride in the presence of caustic soda, triglycerides of the formulæ

$$C_3H_5O \cdot C_7H_5O \begin{cases} O \cdot R \\ \\ O \cdot C_7H_5O \end{cases}$$

and

$$C_3H_5O \cdot R \begin{cases} O \cdot R \\ \\ O \cdot C_7H_5O \end{cases}$$

are obtained.

PAGE 5

α-Monolaurin, $C_3H_5(O.C_{12}H_{23}O)(OH)_2$, prepared by *Krafft*[1] from α-monochlorhydrin and potassium laurate, boils *in vacuo* at 142° C.; it melts at 59° C.

α-Monomyristin, $C_3H_5(O.C_{14}H_{27}O)(OH)_2$, prepared from α-monochlorhydrin and potassium myristate, boils *in vacuo* at 162° C., and melts at about 68° C. (*Krafft*[1]).

α-Monopalmitin.—*Krafft*[1] gives the melting point 72° C.

α-Monostearin.—*Krafft*[1] gives the melting point 78° C.

α-Monoolein.—*Krafft*[1] obtained a product of the melting point 35° C.

PAGE 8

Krafft[1] has shown that in a perfect vacuum trilaurin and trimyristin can be obtained by fractional distillation from laurel oil and nutmeg butter respectively, in such a state of purity that after one recrystallisation

[1] *Berichte*, 1903, 4343

glycerides of normal melting points are obtained. Triglycerides of acids having fourteen carbon atoms seem, however, to form the limit, as experiments made with a view to obtaining tripalmitin from Japan wax did not lead to satisfactory results, owing to decomposition taking place.

PAGE 11

Trilaurin has been obtained by fractional distillation of laurel oil *in vacuo*, and trimyristin in the same manner from nutmeg butter. Trilaurin boils *in vacuo* at 260°-275° C. (*Krafft*[1]). Trimyristin boils *in vacuo* from 290°-300° C. (*Krafft*[1]).

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Lithium laurate,[2] Li $C_{12}H_{23}O_2$, crystallises from alcohol in white shining scales. 100 c.c. of water dissolve at 18° C. 0·158 gram, and at 25° C. 0·176 gram of the salt. 100 c.c. of alcohol of the specific gravity 0·797 dissolve at 18° C. 0·418 gram, and at 25° C. 0·4424 gram of the salt.

The *ethyl-ester* boils *in vacuo* at 79° or 101° C., according as the liquid has to rise 25 mm. or 65 mm.[3]

PAGE 91

Lithium myristate,[2] Li $C_{14}H_{27}O_2$, crystallises from alcohol in the form of small white scales. 100 c.c. of water dissolve at 18° C. 0·0235 gram, and at 25° C. 0·0234 gram of the salt. 100 c.c. of alcohol of the specific gravity 0·797 dissolve at 18° C. 0·184 gram, and at 25° C. 0·22 gram of the salt.

The *ethyl-ester* boils at 295° under ordinary pressure, and *in vacuo* at 102° or 124° C., according as the liquid has to rise 25 mm. or 65 mm. It is sparingly soluble in alcohol and ether, and more readily soluble in petroleum ether.[3]

PAGE 93

Lithium palmitate,[2] Li $C_{16}H_{31}O_2$, crystallises from hot alcohol in small white shining scales. 100 c.c. of water dissolve at 18° C. 0·011 gram, and at 25° C. 0·018 gram of the salt. 100 c.c. of alcohol of the specific gravity 0·797 dissolve at 18° C. 0·0796 gram, and at 25° C. 0·0955 gram of the salt.

The *ethyl-ester* boils *in vacuo* at 122° or 138°, according as the liquid has to rise 25 mm. or 65 mm.[3]

PAGE 95

Lithium stearate,[2] Li $C_{18}H_{35}O_2$, crystallises from alcohol in small white scales. 100 c.c. of water dissolve at 18° C. 0·01 gram, and at 25° C. 0·012

[1] *Berichte*, 1903, 4343. [2] Partheil and Ferié, *Archiv. d. Pharm.* 1903, 545.
[3] Krafft, *Berichte*, 1903, 4340.

gram of the salt. 100 c.c. of alcohol of the specific gravity 0·797 dissolve at 18° C. 0·041 gram, and at 25° C. 0·0532 gram of the salt.

PAGE 96

The *ethyl-ester* boils *in vacuo* at 139° or 154°, according as the liquid has to rise 25 mm. or 65 mm[1].

The *amyl-ester* crystallises from hot alcohol in microscopic white plates of melting point 21° C.

PAGE 106

Lithium oleate,[2] 100 c.c. of water dissolve at 18° C. 0·0674 gram, and at 25° C. 0·132 gram of the salt. 100 c.c. alcohol of the specific gravity 0·797 dissolve at 18° C. 0·9084 gram, and at 25° C. 1·009 gram of the salt.

PAGE 107

The *amyl-ester* of oleic acid is a liquid of the specific gravity 0·897 at 15° C. It does not solidify at 0° C.

[1] Krafft, *Berichte*, 1903, 4340.
[2] Partheil and Ferié, *Archiv. d. Pharm.* 1903, 545.

END OF VOL. I

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